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Sampling and Analysis of the Aquatic Environment in POTW's and Their Vicinity

SCS Engineers, Reston, VA

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16. ABSTRACT

This report presents the result of sampling and analysis of influent, effluent and sludge of publicly owned treatment works (POTWs) and the water and sediment of their receiving waters for 13 heavy metals and 115 synthetic organic compounds (the "priority pollutants" resulting from settlement agreement reprinted in NRDC vs. Train 8 ERC 2120, 2122-29, D.D.C. 1976). The influents to 8 POTWs in Virginia were screened for the priority pollutants, and the Richmond and Culpeper POTWs were revisited for sampling of influent, effluent, sludge and receiving waterbody water and sediment.

At Culpeper 37 priority pollutants were detected and, at Richmond, 34, with 31 common to both sites.

The report contains qualitative and semi-quantitative data on priority pollutant concentrations, and extensive reproductions of GC-MS total ion chromatograms to facilitate comparisons among POTWs.

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DISCLAIMER

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FOREWORD

As a result of litigation under the Clean Water Act, the Environmental Protection Agency has recently been studying intensively 129 "Priority" water pollutants. Most of these pollutants are synthetic organic compounds, whose environmental distribution, persistence and toxicity are still largely unknown.

In an effort to learn more about these pollutants and how to regulate them, EPA has developed state-of-the-art analytical laboratory protocols for determining the presence of these compounds at the very low levels at which they are normally found in the ambient environment. These methods are merely qualitative and semi-quantitative, have not been extensively used, and laboratories using these methods have had little time to develop expertise in their use.

This study, as far as we know, is the first to analyze the influent, effluent and sludge of Publicly Owned Treatment Works (POTWs) for the priority pollutants. Furthermore, the labs performing the analyses had little experience with the procedures. As a result, quantifications should be considered estimates at best, and it is possible that there are false positives and false negatives. With these caveats, however, the study can be used to give one a feeling for which of the priority pollutants are found in the POTW environment.

In order to make this screening study even more useful, the various chromatograms are presented, allowing the reader to draw his own conclusions.

Donald J. Ehreth
Project Officer

1.0 INTRODUCTION

This report presents the results of sampling and analysis of nine publicly owned treatment works (POTWs) for 125 inorganic and organic substances. These substances, together with TCDD, acrylonitrile, Acrolein and asbestos, constitute a group of 129 priority pollutants which are under study by EPA pursuant to a court-ordered settlement agreement in a suit brought by the National Resources Defense Council. The priority pollutants are listed in Table 2.0-1.

The POTWs were selected with the following considerations in mind, so that data acquired might be useful in exposure and fate studies of the priority pollutants:

- Non-tidal discharge so that upstream and downstream concentrations could be compared.
- Likelihood of availability of fish for sampling.
- Activated sludge secondary treatment.
- Location near to Springfield, Virginia laboratory.
- Good chance of finding many of the 125 substances.

A preliminary investigation indicated that the large POTWs in the vicinity are discharging to estuaries, and that most fresh-water located POTWs use trickling filter secondary treatment. Furthermore, it seemed to be difficult to predict at which POTW we would have the best chance of finding priority pollutants.

In consideration of these findings, EPA decided to sample and analyze the influents of 8 POTWs and to then return to one for comprehensive sampling. If the selected POTW did not use activated sludge secondary treatment, we would collect additional influent, effluent and sludge samples from the Richmond POTW. All samples were to be grab samples since we were looking for the presence or absence of pollutants, rather than attempting to construct a mass balance.

The Culpeper plant was eventually selected for intensive sampling. Since the Culpeper POTW was a trickling filter secondary, the Richmond

plant was also sampled. At Culpeper, the upstream and downstream aquatic environments were sampled for evidence of the POTW's impact.

2.0 SUMMARY

At the Culpeper facility a total of 37 priority pollutants were observed in the samples taken. These included:

- 4 pesticides.
- 12 metals.
- 11 volatile organics.
- 1 acid extractable semi-volatile organic.
- 7 base-neutral extractable semi-volatile organics.
- cyanide.
- total phenolics.

At Richmond, 34 compounds appeared:

- 4 pesticides.
- 12 metals.
- 9 volatile organics.
- 1 acid extractable semi-volatile organic.
- 6 base-neutral extractable semi-volatile organics.
- cyanide.
- total phenolics.

Of these compounds, 31 were common to both plants.

Major observations which were made:

- The priority pollutants observed during these analyses in influent, effluent, sediment or sludge at at least one of the 9 sites are indicated in Table 2.0-1.
- The VOA (volatile organic analysis) contents of the Culpeper sludge and effluent are considerable, while those of Richmond are greatly diminished. This appears to be the result of the increased biodegradation occurring in the activated sludge as well as the improved opportunity for volatilization of these compounds.
- The metal data exhibit the established tendency of metals following the solid surfaces and becoming enriched in the sludge.
- The pesticides seem to parallel the metals at Richmond, but limited data at Culpeper does not allow that conclusion.

- Neither acid nor base-neutral extractables were abundant at either site.
- The effect of the Culpeper plant on downstream water quality is demonstrable, but at near detection limit levels. Further detailed work would be required to refine the analytical and sampling techniques to be able to point out differences between upstream and downstream points.
- A set of Culpeper influent VOA duplicate samples were stored under protocol (1,2) conditions for 6 weeks. They were analyzed weekly. Within a ± 20% bandwidth, the data was stable over the first 4 weeks of storage.

TABLE 2.0-1

LIST OF 129 PRIORITY POLLUTANTS

CAS NO.	DETECTED IN THIS STUDY	PRIORITY POLLUTANT	DETECTION LIMIT (ppb)*
		GENERAL INORGANICS	
57125	X	CYANIDE, TOTAL	5
1332214	NA	ASBESTOS (FIBROUS)	-
METALS			
7439921	X	LEAD, TOTAL	50
7439976	X	MERCURY, TOTAL	0.2
7440020	X	NICKEL, TOTAL	20
7440224	X	SILVER, TOTAL	10
7440280		THALLIUM, TOTAL	100
7440360	X	ANTIMONY, TOTAL	200
7440382	X	ARSENIC, TOTAL	2
7440417	X	BERYLLIUM, TOTAL	5
7440439	X	CADMIUM, TOTAL	2
7440473	X	CHROMIUM, TOTAL	20
7440508	X	COPPER, TOTAL	10
7440666	X	ZINC, TOTAL	5
7782492	X	SELENIUM, TOTAL	2
		GENERAL ORGANICS	
PHENOLS AND CRESOLS			
UNKNOWN	X	PHENOLICS, TOTAL, RECOVERABLE (UG/L)	20
51285		2,4-DINITROPHENOL	1000
59507		PARACHLOROMETA CRESOL	50
87865		PENTACHLOROPHENOL	50
88062		2,4,6-TRICHLOROPHENOL	50
88755		2-NITROPHENOL	50
95578		2-CHLOROPHENOL	50
100027		4-NITROPHENOL	50
105679		2,4-DIMETHYLPHENOL	50
108952		PHENOL (C6H50H)-SINGLE COMPOUND	50
120832		2,4-DICHLOROPHENOL	50
534521		4,6-DINITRO-ORTHO-CRESOL	1000

* - For aqueous matrix samples.

TABLE 2.0-1 (Continued)

GENERAL ORGANICS - (Cont'd.)

CAS NO.	DETECTED IN THIS STUDY	PRIORITY POLLUTANTS	DETECTION LIMIT (ppb)
ETHER			
101553		4-BROMOPHENYL PHENYL ETHER	10
110758		2-CHLOROETHYL VINYL ETHER	10
111444		BIS (2-CHLOROETHYL) ETHER	1
111911		BIS (2-CHLOROETHOXY) METHANE	10
542881		BIS (CHLOROMETHYL) ETHER	1
7005723		4-CHLOROPHENYL PHENYL ETHER	10
39638329		BIS (2-CHLOROISOPROPYL) ETHER	10
HALOGENATED ALIPHATICS			
56235	X	CARBON TETRACHLORIDE	1
67663	X	CHLOROFORM	1
67721	X	HEXACHLOROETHANE	10
71556	X	1,1,1-TRICHLOROETHANE	1
74839		METHYL BROMIDE	1
74873		METHYL CHLORIDE	1
75003	X	CHLOROETHANE	1
75014		VINYL CHLORIDE	1
75092	X	METHYLENE CHLORIDE	1
75252		BROMOFORM	1
75274	X	BROMODICHLOROMETHANE	1
75343	X	1,1-DICHLOROETHANE	1
75354	X	1,1-DICHLOROETHYLENE	1
75694	X	TRICHLOROFLUOROMETHANE	1
75718		DICHLORODIFLUOROMETHANE	1
77474		HEXACHLOROCYCLOPENTADIENE	10
78875		1,2-DICHLOROPROPANE	1
79005		1,1,2-TRICHLOROETHANE	1
79016	X	TRICHLOROETHYLENE	1
79345		1,1,2,2-TETRACHLOROETHANE	1
87683		HEXACHLOROBUTADIENE	10
107062		1,2-DICHLOROETHANE	1
124481		DIBROMOCHLOROMETHANE	1
127184	X	TETRACHLOROETHYLENE	1
156605	X	1,2-TRANS-DICHLOROETHYLENE	1
542756		1,3-DICHLOROPROPENE	1

TABLE 2.0-1 (Continued)

GENERAL ORGANICS - (Cont'd.)

CAS NO.	DETECTED IN THIS STUDY	PRIORITY POLLUTANT	DETECTION LIMIT (ppb)
POLYCYCLIC AROMATIC HYDROCARBONS			
50328		BENZO-A-PYRENE	10
53703		1,2,5,6-DIBENZATHRACENE	10
56553		BENZO(A)ANTHRACENE	10
83329		ACENAPHTHENE	10
85018		PHENANTHRENE	10
86737		FLUORENE	10
91203	X	NAPHTHALENE	10
120127		ANTHPACENE	10
129000	X	PYRENE	10
191242		BENZO(GHI)PERYLENE	10
193395		INDENO (1,2,3-CD)PYRENE	10
205992		BENZO(B)FLUORANTHENE	10
206440		FLUORANTHENE	10
207089		BENZO(K)FLUORANTHENE	10
208968		ACENAPHTHYLENE	10
218019		CHRYSENE	10
MONOCYCLIC AROMATICS			
71432	X	BENZENE	1
95501	X	1,2-DICHLOROBENZENE	10
98953		NITROBENZENE	10
100414	X	ETHYLBENZENE	1
106467	X	1,4-DICHLOROBENZENE	10
108883	X	TOLUENE	1
108907		CHLOROBENZENE	1
118741		HEXACHLOROBENZENE	10
120821		1,2,4-TRICHLOROBENZENE	10
121142		2,4-DINITROTOLUENE	10
541731		1,3-DICHLOROBENZENE	10
606202		2,6-DINITROTOLUENE	10

TABLE 2.0-1 (Continued)

GENERAL ORGANICS - (Cont'd.)

CAS NO.	DETECTED IN THIS STUDY	PRIORITY POLLUTANTS	DECTECTION LIMIT (ppb)
NITROSAMINES AND OTHER N COMPOUNDS			
62759		N-NITROSODIMETHYLAMINE	10
86306		N-NITROSODIPHENYLAMINE	10
91941		3,3'-DICHLOROBENZIDINE	10
92875		BENZIDINE	10
107131		ACRYLONITRILE	-
122667		1,2-DIPHENYLHYDRAZINE	10
621647		N-NITROSODI-N-PROPYLAMINE	10
PCBs AND RELATED COMPOUNDS			
91587		2-CHLORONAPHTHALENE	10
11096825		AROCLOR 1260 PCB SERIES	~1
11097691		AROCLOR 1254 PCB SERIES	~1
11104282		AROCLOR 1221 PCB SERIES	~1
11141165		AROCLOR 1232 PCB SERIES	~1
12672296		AROCLOR 1248 PCB SERIES	~1
12674112		PCB-1016	~1
53469219		AROCLOR 1242 PCB SERIES	~1
PHTHALATE ESTERS			
84662	X	DIETHYL PHTHALATE	10
84742	X	DI-N-BUTYL PHTHALATE	10
85687		N-BUTYL BENZYL PHTHALATE	10
117817	X	BIS(2-ETHYLHEXYL)PHTHALATE	10
117840		DI-N-OCTYL PHTHALATE	10
131113	X	DIMETHYL PHTHALATE	10
PESTICIDES			
7421934		ENDRIN ALDEHYDE	1
50293		P,P'-DDT	1
57749		CHLORDANE (TECH MIX & METABS)	1
58899		GAMMA-BHC (LINDANE)	1
60571	X	DIELDRIN	1
72208	X	ENDRIN	1
72548		P,P'-DDD	1
72559	X	P,P'-DDE	1
76448		HEPTACHLOR	1

TABLE 2.0-1 (Continued)

GENERAL ORGANICS - (Cont'd.)

CAS NO.	DETECTED IN THIS STUDY	PRIORITY POLLUTANTS	DETECTION LIMIT (ppb)
PESTICIDES (Cont'd).			
78591		ISOPHORONE	1
107028		ACROLEIN	-
309002		ALDRIN	1
319846	X	ALPHA BHC	1
319857	X	BETA BHC	1
319868		DELTA BHC	1
959988	X	ENDOSULFAN, ALPHA	1
1024573		HEPTACHLOR EPOXIDE	1
1031078		ENDOSULFAN SULFATE	1
1746016	NA	2,3,7,8-TETRACHLORODIBENZO-P-DIOXIN (TCDD)	-
8001352		TOXAPHENE	1
33213659		ENDOSULFAN, BETA	1

NA - NOT ANALYZED

3.0 EIGHT SITE SCREENING

Eight POTWs located in Virginia were chosen to be sampled for 125 priority pollutants. They represented a range of influent types from heavily industrial to mostly residential. Table 3.0-1 compares their various characteristics. Fig. 3.0-1 places each plant in its drainage basin.

A tabulation of industries sited in the 8 cities is provided as Appendix D. No information was gathered as to which did or did not discharge to the POTW.

A two man field crew was used consisting of G. Vogel from Versar and J. Erlandson of SCS Engineers. This team prepared the sample containers and gathered the required coolant for cold storage of the samples. After coordination with Mr. Ort Villa, Director of EPA Region III Laboratory, arrangements were made with each of the POTW operators for access to the plants.

It was decided by the EPA Task Manager to obtain grab samples of influent to assess the priority pollutant loading to each plant. Based on the analytical results, a choice would be made of a plant with both a wide range and meaningful concentrations of priority pollutants.

In the interests of rapid identification of the most interesting site, we were directed to scan the influent extracts by gas chromatography using the Flame Ionization Detector (FID). The same extracts would be rerun prior to completion of the program on GC/MS instrumentation which would allow storage of the raw data on magnetic tape for later analysis of other than the 125 pollutants.

3.1 Field Sampling

The only departure from the original plan was substitution of a second Charlottesville facility for the Salem installation. Contact with the managers concerned indicated that the Salem operation was in fact a pumping station which fed the Roanoke POTW. This change to the 8 site screening was authorized by the EPA Task Manager.

Delayed due to rainstorms, sampling at the eight sites occurred on December 6 and 7, 1977.

Specific details of the sampling techniques, equipment and preservation methods are in all respects those procedures recommended by the Agency for the proper handling of priority pollutant samples. (1,2)

TABLE 3.0-1

Eight Site Screening POTWs

Location	Flow at Sampling (mgd)	Avg. Flow (mgd)	% Flow from Industrial Discharge *	Width of Receiving Stream (ft)	Stream Depth (ft)	Trickling Filter/ Activated Sludge	Anaerobic Dig.
Roanoke	37	21	50	35	10	TF/AS	Yes
Lynchburg	20.5	15	15	125	20-30	TF/AS	No
Charlottesville Meadow Creek	3.7	3.0	14	15	0.5	TF	Yes
Charlottesville Moore's Creek	5.3	2.8	10	20	1-2	TF/AS	Yes
Waynesboro	3.9	2.8	50	35	2	TF	Yes
Staunton	2.6	1.8	20	15	0.5	TF	Yes
Harrisonburg	6.76	4.75	40	70	4-10	AS	Yes
Culpeper	1.9	1.1	20	36	1-2	TF	Yes
Richmond	70	70	?	200	8-10	AS	Yes

* Estimate obtained from plant operator.

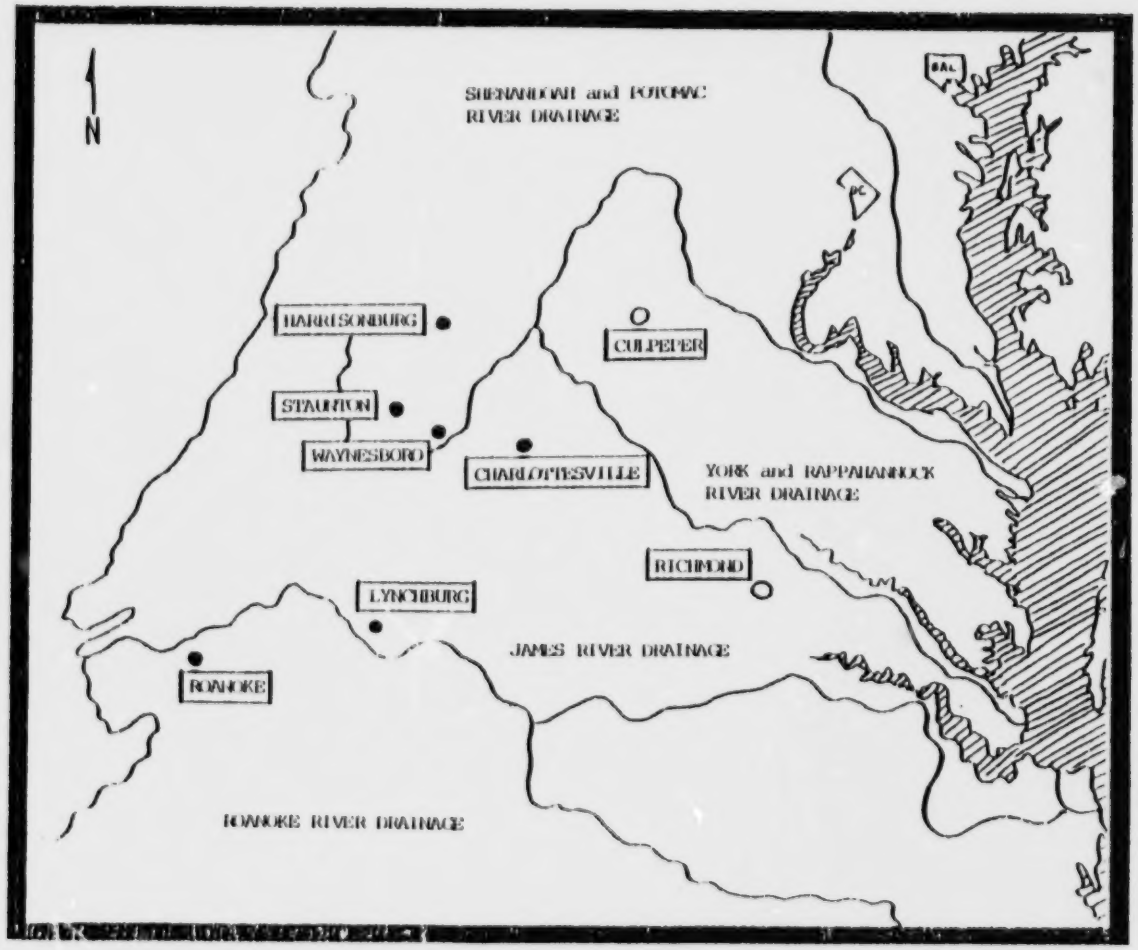

Figure 3.0-1

POTW Sites And Associated

Drainage Basins

3.2 Site Descriptions

Each treatment plant was visited and an influent grab sample obtained. The receiving stream was surveyed to assess the effort involved in later effluent and environmental sampling. The following are descriptions of each facility.

3.2.1 Roanoke

The Roanoke sewage treatment plant was the only tertiary plant sampled. Tertiary facilities include nitrification and phosphate removal. Aeration basins and anaerobic digesters are employed in the secondary treatment portion of this plant. Alum, chlorine, and steel mill acid are added during the treatment process. An estimated 50 percent of the influent is from industrial dischargers. The average flow for 1977 is about 23 MGD, with 33 MGD for November. Influent sample was obtained on December 6 at 8:30 a.m. when the flow was approximately 37 MGD. This plant receives sewage from several small communities in the area, including Salem. The outfall from the Roanoke plant is at surface level of the Roanoke River, which is approximately 35 feet wide and 10 feet deep at this point. The water was quite turbid above and below the outfall. Access to the outfall and river would be no problem for subsequent sampling.

3.2.2 Lynchburg

The Lynchburg is a secondary sewage treatment facility employing aeration basins, heat treatment and centrifugation of sludge. This was the only plant sampled that used this sludge treatment instead of anaerobic digestion. Ammonia and chlorine are added during the treatment process. An estimated 15% of the influent is from industrial dischargers, including paper mills, electric component manufacturing, paper product production, printing, and electro-plating operations. The average flow is from 10 to 12 MGD with a mean flow for November 1977 of 15 MGD. The flow at sampling was 20.5 MGD on December 6 at 11:30 a.m. The discharge from the Mead Paper Company goes through primary treatment at the Lynchburg plant in separate facilities. The wastes from these facilities enter the Lynchburg municipal treatment system below the point from which the sample was taken.

The outfall from the Lynchburg plant is about two feet below the surface level of the James River, which is about 20-30 feet deep and 125 feet wide at this point and is quite turbid. Access to the outfall is difficult as it requires crossing a ditch and a C&O Railroad switchyard.

3.2.3 Charlottesville - Meadow Creek Plant

This Charlottesville plant is a secondary sewage treatment facility employing trickling filters and anaerobic digesters. Alum, polymers, and chlorine are added during the treatment process. An estimated 14 percent of the influent is from industrial dischargers, including electric component manufacturing, laundry and dairy wastes. Average flow is about 3.0 MGD. Influent sample was obtained December 6 at 2:15 p.m. when the flow was 3.7 MGD. Overflow from a recent storm was being taken from storage and entered into the system at the time of sampling. The outfall is about three feet above the surface of Meadow Creek which is 10-15 feet wide and 6 inches deep. Access to this relatively clean stream is no problem for subsequent sampling.

3.2.4 Charlottesville - Moore's Creek

This Charlottesville plant is a secondary treatment facility with trickling filters and anaerobic digester. Alum, polymer, and chlorine are added during the treatment process. An estimated 10 percent of the plant influent is from industrial dischargers, including laundry and dairy wastes. Average flow is about 2.8 MGD. The influent sample was obtained December 6 at 3:30 p.m. when the flow was 5.3 MGD. It was taken from a point which contained some return supernatant. This was necessary to include discharge from a commercial laundry. The outfall is at surface level at Moore's Creek which is 15 to 25 feet wide and 1 to 2 feet deep at this point. Moore's Creek was somewhat turbid when visited, possibly due to storm runoff. Access to outfall would be no problem for subsequent sampling.

3.2.5 Waynesboro

The Waynesboro plant is a secondary treatment facility with trickling filters and anaerobic digesters. Chlorine and o-dichlorobenzene (*) are added during the treatment process. An estimated 50 percent of the influent is from industrial dischargers, including furniture manufacturing, plating, metal fabrication, and electric component manufacturing wastes. The DuPont plant treats its own industrial waste. The average flow is 2.75 MGD. The flow at sampling was 3.88 MGD on December 7 at 10:00 a.m. The outfall from the Waynesboro plant is approximately 2 feet above the South River which is about 35 to 40 feet wide and one to two feet deep at this point. The South River is relatively clean above and below the outfall, and access would be no problem in subsequent sampling.

3.2.6 Staunton

The Staunton plant is a secondary treatment facility with trickling filters and anaerobic digesters. Chlorine is added during the treatment process. An estimated 20 percent of the influent is from industrial dischargers, including plating, dairy and laundry wastes. Average flow is 1.75 MGD. Influent sample was obtained on December 7 at 11:30 a.m. when the flow was 2.6 MGD. Work is in progress to upgrade and expand this plant.

The outfall from the Staunton plant is level with receiving stream which is 10 to 15 feet wide and 6 inches deep. This stream is relatively clean upstream and access for subsequent sampling would be no problem.

3.2.7 Harrisonburg

The Harrisonburg-Rockingham plant is a secondary treatment facility with aeration tanks and anaerobic digesters. Chlorine is added during the treatment process. An estimated 40 percent of the influent is from industrial dischargers, including dairy and poultry processing wastes. Average flow is 4.75 MGD. Influent sample was obtained December 7 at 2:30 p.m. when the flow was 6.75 MGD. This new waste water treatment plant also receives sewage from several small communities in the area.

(*) Though ortho-dichlorobenzene is one of the 129 priority pollutants, it has a major application as an "odor masking" agent in POTWs.

The outfall to the North River is a cascade approximately 100 meters long. The North River is approximately 50 feet wide and 4 to 10 feet deep and quite turbid at this point. Access would be no problem for subsequent sampling.

3.2.8 Culpeper

The Culpeper plant is a secondary treatment facility with trickling filters and anaerobic digesters. Chemical addition during the treatment process includes $FeCl_3$, polymers, and chloride. An estimated 15 to 20 percent of the influent is from industrial dischargers, including wire mill, laundry and flour mill wastes. Average flow for 1977 is 1.1 MGD. Influent sample was obtained December 7 at 5:00 p.m. when the flow was 1.9 MGD.

The outfall from the Culpeper plant is about 1-1/2 feet above the receiving stream, which is about 15 to 20 feet wide and 1 to 2 feet deep. The stream was quite turbid, possibly from storm runoff. A small aeration dam is located about 20 feet upstream of the outfall. Access would be no problem for subsequent sampling.

3.3 Analysis

3.3.1 Volatile Organics

The samples were analyzed using published EPA procedures. (1,2) Table 3.3.1 gives the observed volatiles as a range over the eight POTWs.

3.3.2 Base-Neutral Extractable Semi-Volatile Organics

The base-neutral extractable semi-volatile organics observed in the analysis of the influent screening samples are given in Table 3.3.2. Both GC/FID and GC/MS data have been placed in the table. GC/FID chromatograms and GC/MS total ion chromatograms are found in Appendix A.2 for these samples.

3.3.3 Acid Extractable Semi-Volatile Organics

GC-FID analysis were not accomplished on the screening samples due to problems with the Tenax GC columns. Subsequent GC/MS runs on the acid extracts identified none of the acid extractables on the priority pollutant list. The GC/MS total ion chromatograms for the screening samples appear in Appendix A.3.

Table 3.3.1

Volatile Organics Observed in GC-FID Screening Analysis of 8 POTW Influent Streams

Compound	No. of Occurrences	Range
Benzene	5	Susp. * - 10 ppb
Chloroethane	1	8 ppb
Chloroform	1	Susp. *
Dichloroethylene	1	Susp. *
Ethyl Benzene	5	Susp. * - 20 ppb
Tetrachloroethane	3	Susp. - 10 ppb
Trichloroethylene	3	Susp. - 10 ppb
Trichlorofluoromethane	1	Susp.
Toluene	8	0.88 - 20 ppb

* Susp. = Suspected

Section A.1 of Appendix A provides information on the conditions of analysis as well as VOA chromatograms from all the screening samples.

Table 3.3.2

Base-Neutral Extractable Semi-Volatile Organics Observed In GC/FID and GC/MS Analysis of 8 POTW Influent Streams

Compound	No. of Occurrences	Range
Dimethyl Phthalate	3	40 - 2800 ppb
bis (2-ethylhexyl) phthalate	6	<20 - 7100 ppb
Di-n-butyl phthalate	3	<20 - 260 ppb
Pyrene	1	320 ppb
Trichlorobenzene	1	200 ppb
Naphalene	3	<20 ppb

Section A.2 of Appendix A provides the conditions of analysis as well as GC/FID chromatograms

3.3.4 Total Phenolics

The wet chemistry test for total phenolics considers them to be hydroxyderivatives of benzene and its condensed nuclei. The total phenolics ranged from 30 ppb in the Harrisonburg influent to 110 ppb in the Charlottesville, Meadow Creek influent. The data for each stream is tabulated in Appendix A.4.

3.3.5 Cyanide

Each of the 8 influents contained a measurable quantity of cyanide. They ranged from 5 ppb at Staunton to 110 ppb at Lynchburg. The data for each stream is tabulated in Appendix A.5.

3.3.6 Metals

The 8 influent samples were analyzed for metals. All metals were identified with the exception of thallium. Summary Table 3.3.3 shows the ranges encountered. The influent screening sample metals were analyzed under the direction of SCS Engineers.

Table 3.3.3

Metals in Influent Samples (ppb)*

Metal	No. of Occurrences	Range
Antimony	2	2 - 4
Arsenic	4	1 - 35
Beryllium	5	.01 - .05
Cadmium	8	.5 - 20.6
Chromium	9	5 - 300
Copper	9	18 - 190
Lead	9	13 - 610
Mercury	3	1 - 10
Nickel	9	1 - 150
Selenium	7	2 - 4
Silver	5	0.6 - 12
Thallium	0	(<2)
Zinc	9	60 - 540

*Total is 9 samples since two samples from Harrisonburg were analyzed.

A complete table of influent analyses is to be found in Appendix A.6.

3.3.7 Pesticides

Pesticides were analyzed by GC with the electron capture detector. Only three pesticides were observed, none in a high enough concentration to be confirmed by GC/MS. See Table 3.3.4 below:

Table 3.3.4

Pesticides in Influent Screening Samples

Pesticide	No. of Occurrences	Range (ppb)
B-BHC	1	1
Heptachlor or aldrin	1	1
Heptachlor or aldrin	1	1

Section A.7 of Appendix A provides the GC/EC chromatograms for the samples.

3.4 Choice of Site for Intensive Sampling

The data gathered in Section 3.3 was used as a basis for choosing the site for intensive sampling. Under the direction of the EPA the Culpeper POTW was chosen. The choice was based on the existence of a wide range of compounds as exhibited by the chromatograms, as well as a number of specific compounds which occurred at considerable concentrations. Toluene at 9 ppb is an example.

Since the Culpeper POTW uses trickling filter secondary treatment, EPA decided to collect and analyze samples of the Richmond POTW's influent, effluent and sludge to supplement the Culpeper data. The Richmond POTW uses activated sludge secondary treatment.

The conditions at the Culpeper facility were such that biological sampling for fish and benthos did not produce significant results. The receiving stream was extremely small. Though typically 6% of the stream flow was from the plant, little impact was noted in the observable ecology of the stream. Details of the biological sampling are contained in Section 4.2 of this report.

4.0 TWO-SITE INTENSIVE SAMPLING

The Culpeper POTW and the Richmond POTW were chosen after discussion of the screening results. The two sites offered the chance to make some comparisons as follows:

Small vs. Large POTW
Trickling Filter vs Activated Sludge Treatment

The grab-sampling approach was adopted with the full realization that the data so gained should be used with caution for even back-of-envelope mass balance calculations.

4.1 Field Sampling

4.1.1 Culpeper POTW

Samples were obtained at the Culpeper POTW on March 20, 1978. The sludge was obtained at the discharge to the drying beds. No dried sludge was taken. The influent sample was taken immediately upstream from the bar screens. The effluent was taken at the outfall into Mountain Run. Attached as Figure 4.1.1-1 is a schematic of the Culpeper Plant with the sampling points indicated. The location of the Culpeper POTW with respect to the immediate vicinity is shown in Figure 4.1.1-2. The flow of the receiving stream, Mountain Run, is from left to right on the figure. Mountain Run eventually joins the upper reach of the Rappahannock River halfway between Culpeper and Fredericksburg, Va. as shown in Figure 4.1.1-3.

On the day of sampling, the effluent made up approximately 6% of the Mountain Run flow at the downstream rectangular weir where the downstream water and sediment samples were taken. There is no reason to assume the effluent was completely mixed into the receiving stream at the downstream weir. Observations of a soapy surface layer indicated the effluent was remaining quite coherent, slightly to the outside of the center line of the stream at the sampling point. The samples were taken in the "effluent-rich" area so as to

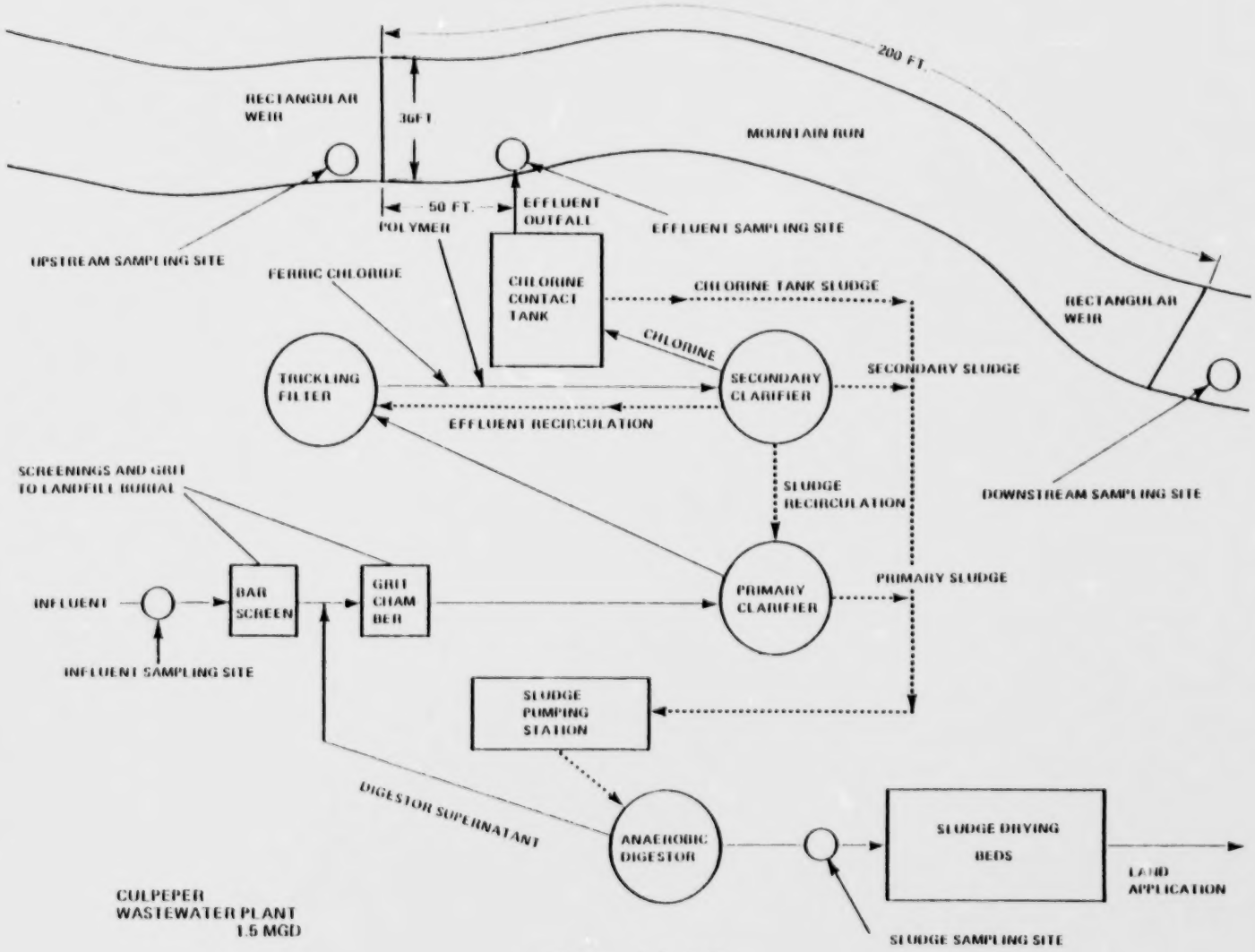

Figure 4.1.1-1

Schematic of the Culpeper Plant

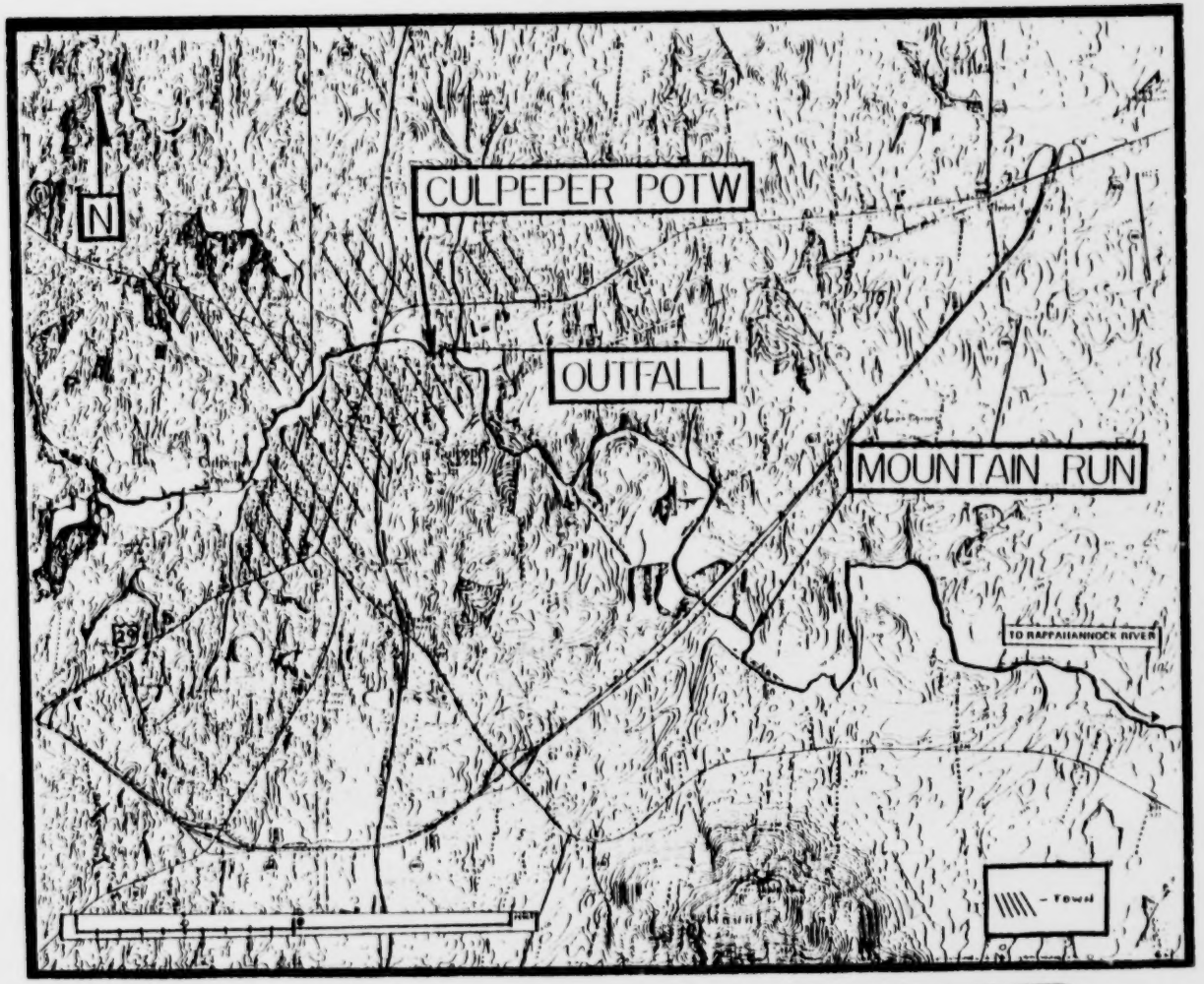

Figure 4.1.1-2

Culpeper POTW Environs

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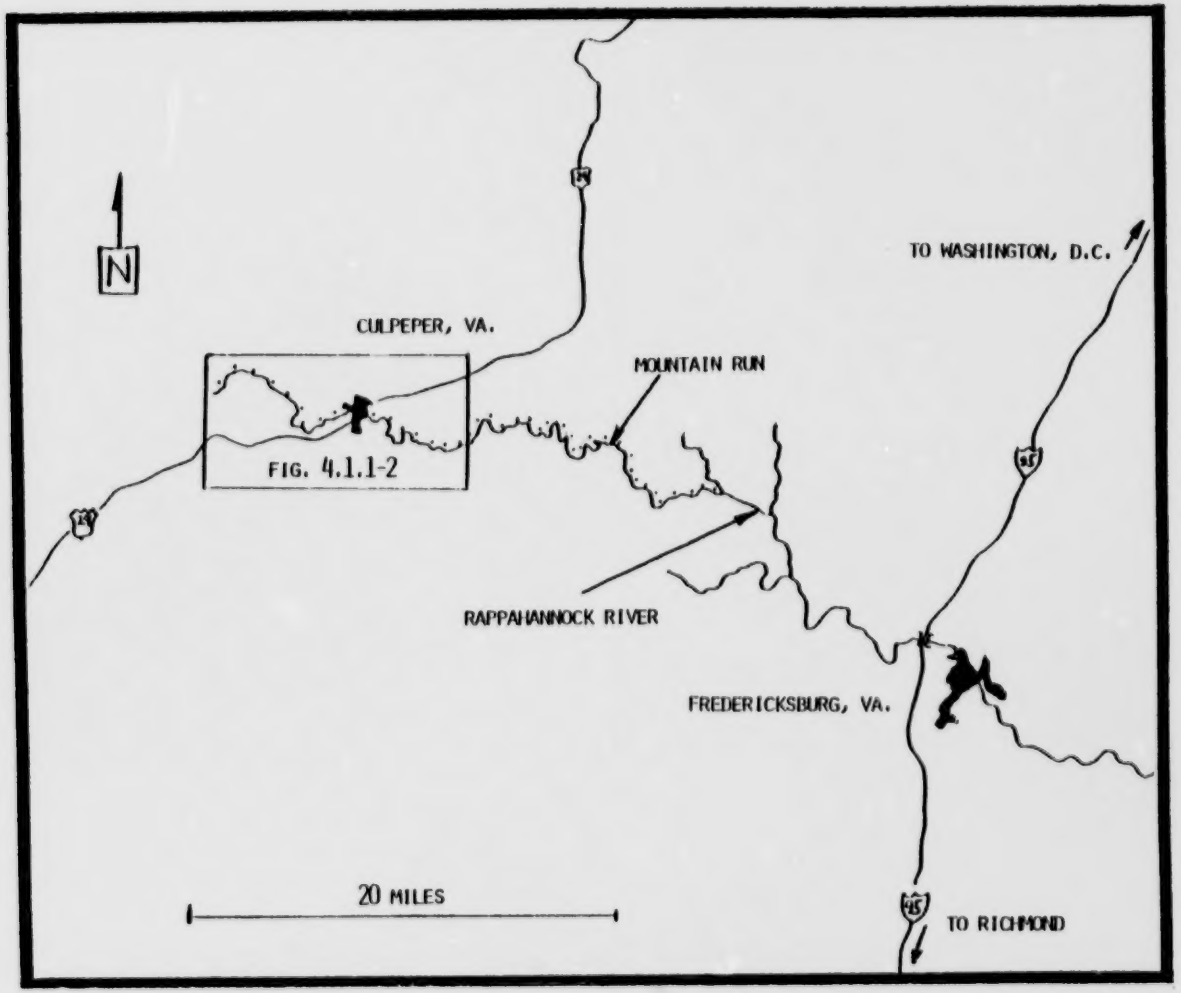

Figure 4.1.1-3
Rappahannock River Drainage Basin

provide a worst case analysis. The upstream samples of water and sediment were gathered adjacent to a second rectangular weir, sited above the effluent outfall.

4.1.2 Richmond POTW

Figure 4.1.2-1 provides an overview of the Richmond facility. The average flow of the plant is 70 mgd and is a series operation of primary clarification, and activated sludge. This is followed by secondary clarification where the effluent is contacted with chlorine and introduced to the James River. The sludge undergoes digestion, is dewatered and sent to drying beds.

A 3 point sampling was accomplished at Richmond. The influent sample was taken just upstream of the grit chamber. The effluent sample was obtained after chlorination at the outlet chamber discharging to the James River. The sample of wet sludge was obtained at the pumping stage to the vacuum filters. The location of the plant with respect to the James River is presented in Figure 4.1.2-2. The general area around Richmond and Petersburg is shown in Figure 4.1.2-3. The James River broadens significantly downstream of the Town of Bermuda Hundred. The flow velocity drops and residence times for waterborne contaminants can increase significantly at a given point.

All samples were preserved, transported and analyzed in accordance with EPA protocols.[1,2]

4.2 Biological Sampling

Benthic Community in Mountain Run, Culpeper, Va.

Benthic macroinvertebrates in Mountain Run were sampled using a Surber net. It was originally intended to sample both above and below the POTW outfall, but the long slow reach above the outfall did not provide suitable substrate or current conditions for use of the Surber net. Although current speed increases below the outfall, the steep drop-off from the streambank makes sampling difficult, and as a result only 11 organisms were collected in several trials. Of these, six were tubificid worms, three were chironomid larvae, one was a caddis-fly larva (Hydropsyche sp.), and one was a Simulium pupa.

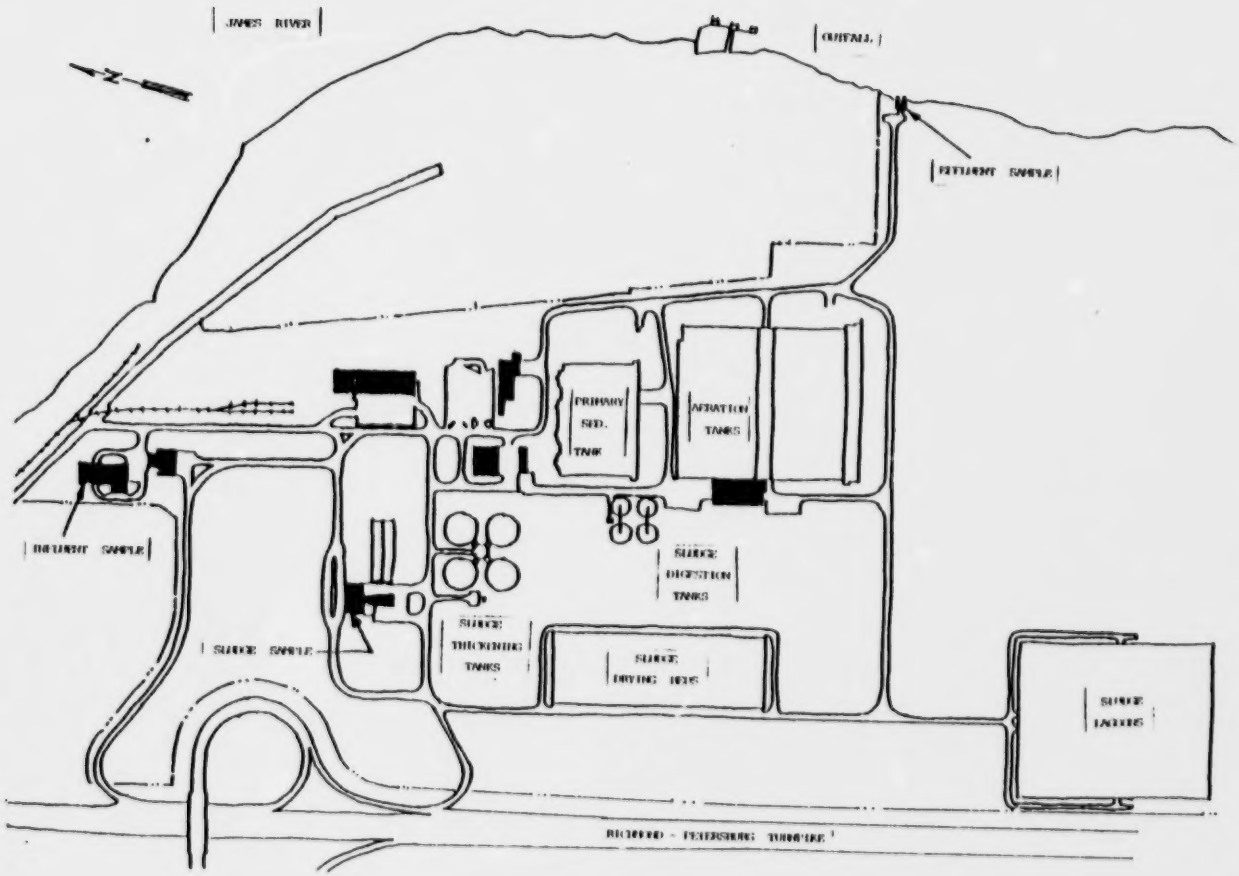

Figure 4.1.2-1

Schematic Of Richmond POTW

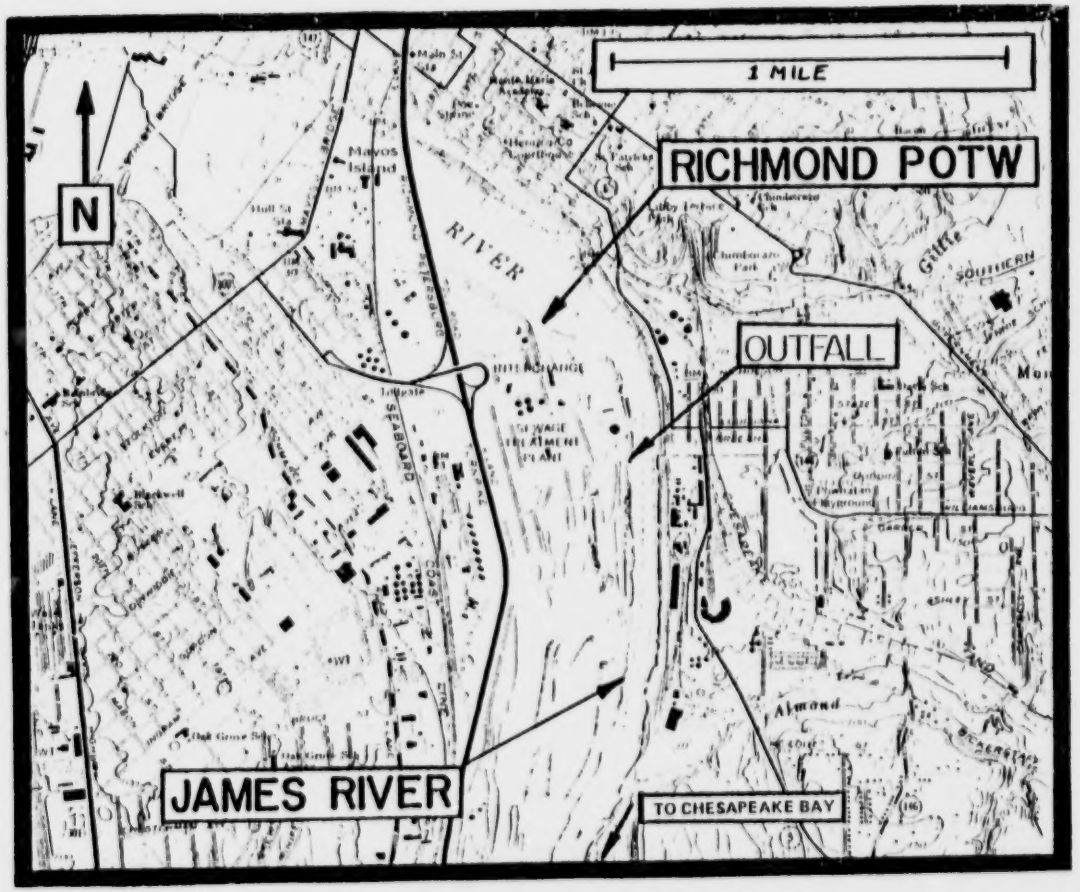

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Figure 4.1.2-2

Richmond POTW and Immediate Vicinity

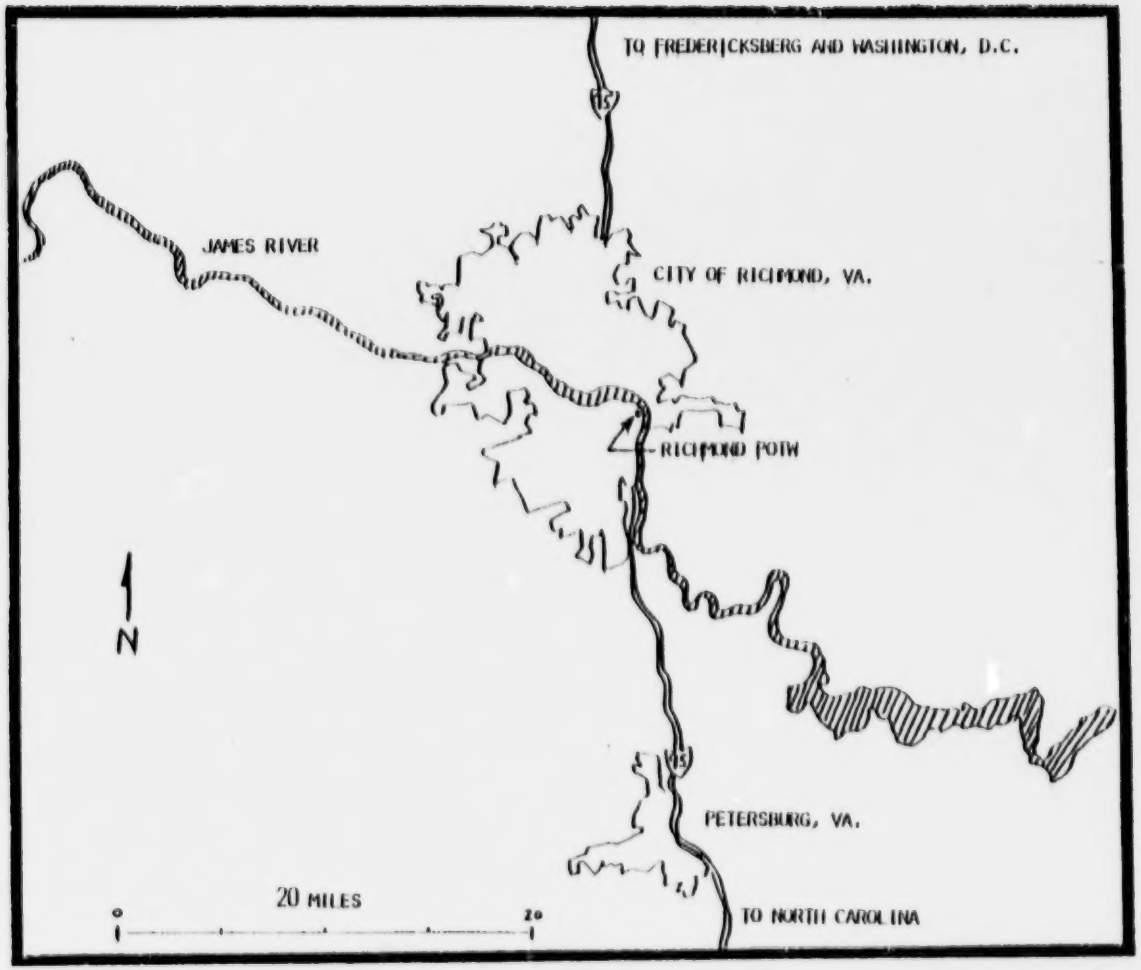

Figure 4.1.2-3
Richmond Environs

The two most common forms, the tubificids and chironomids, are characteristic of waters polluted by organic wastes. Most of the species in these families are quite tolerant to such pollution, and can survive and flourish under conditions which would be lethal to most other benthic invertebrates. Although found in great densities in polluted water, these organisms are, of course, also found in unpolluted environments, but their relative abundance is considerably smaller.

The presence of the two other organisms indicates that water quality in the creek may not be critically impacted by the STP effluent. Weber (1973) compiled data on the tolerance of benthic invertebrates to organic pollution and found that most caddis-fly larvae of the family Hydropsychidae are tolerant to moderate, but not extreme levels of organic contamination.[3] Simulid larvae are also unable to survive in conditions of extreme organic pollution. Thus, the fact that these organisms were found less than 50 m downstream from the outfall indicates that dissolved oxygen, toxic pollutant, and suspended solids levels do not exceed the tolerance limits for these web spinning invertebrates. It is also possible that downstream drift of these organisms accounts for their presence in the samples.

It is important to emphasize that analysis based on such a small sampling size (n = 11) is sheer speculation; any firm conclusions on the effect of the STP outfall on the benthic community must await sampling of both upstream and downstream sites.

4.3 Analytical Results

The present task uses new analytical methodology-laboratory protocols which have not been tested sufficiently through extensive experimentation. The protocols are based on some laboratory experience and are presently considered by EPA to be the best analytical approach available. QC efforts in this undertaking have centered on measurements of precision rather than accuracy. It has been demonstrated that interlaboratory comparisons exhibit wide variations in measured concentrations (7).

In the present task we take note of the analytical uncertainties. In addition, we must realize that a POTW is a very dynamic system with each unit process having different time constants for water, solids, and probably each analyte. Hence the synoptic picture presented here should be viewed in general terms. The matrix differences between influent-effluent-sludge can produce artifacts that may hide or bias real trends. Any thought to doing a rigorous mass balance on any compound with only those three components measured is inappropriate.

Neither should the analytical results presented here be used as a basis for quantitative extrapolation.

Attached as Table 4.3-1 is the tabulated data for the two plants.

Data near the detection limits has been indicated in several ways. These are:

ND - Not detected, no qualitative indication of the compound of interest.

<A - Compound suspected in concentration <A, but could not confirm.
For example, a GC/MS scan might only yield 1 or 2 of the 3 required characteristic ions at the specified retention time window.

The preceding discussion strongly suggests that understanding the effect of unit processes in a POTW requires an intensive sampling program. The present study was structured to provide a before and after snapshot of the existing priority pollutants. Consideration of the complex dynamics of such a system makes us cautious in extrapolating too far from the actual data obtained.

This simple exercise provides ample warning against undue dependence on the analytical results from the grab sampling accomplished in this task. A much more detailed knowledge of the plant and its unit processes is required to allow generalizing about the fate of priority pollutants.

Table 4.3-1

Concentration of Priority Pollutants in POTW Samples[1]

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CAS No.	Compound Name	Richmond POTW Influent	Richmond POTW Effluent	Richmond POTW Sludge	Culpeper POTW Influent	Culpeper POTW Effluent	Culpeper POTW Sludge	Water Upstream	Water Downstream	Sediment Upstream	Sediment Downstream
	VOLATILES										
71-43-2	Benzene	11	ND	<1	3	1	4	ND	<1	ND	ND
75-27-4	Bromodichloromethane	ND	ND	ND	2.5	ND	ND	ND	ND	ND	ND
67-66-3	Chloroform	13	4.5	ND	25	6	ND	ND	1	ND	ND
75-34-3	1,1 Dichloroethane	1	ND	5	ND	ND	6	ND	ND	ND	ND
100-41-4	Ethyl Benzene	11	ND	9	14	16	230	ND	ND	ND	ND
75-09-2	Methylene Chloride	33	10	20	ND	ND	<1	ND	ND	ND	ND
127-18-4	Tetrachloroethylene	84	6	8	157	125	3	ND	3	ND	ND
108-88-3	Toluene	46	ND	93	29	3.5	390	ND	<1	ND	ND
156-60-5	1,2 Trans Dichloroethylene	ND	ND	ND	ND	ND	5	ND	ND	ND	ND
71-55-6	1,1,1-Trichloroethane	78	ND	ND	1.5	ND	200	ND	ND	ND	ND
79-01-6	Trichloroethylene	5.5	1	2	3	1	3	ND	ND	ND	ND
	BASE-NEUTRALS										
117-81-7	bis(2-ethylhexyl)phthalate	>100	91	2795*	ND	ND	41	27	ND	1.4	101
85-68-7	Butyl benzyl phthalate	30	20	ND	ND	ND	ND	ND	ND	ND	ND
84-74-2	Di-n-butyl phthalate	64	45	ND	<20	ND	ND	ND	ND	ND	ND
84-66-2	Diethyl phthalate	>100	87	ND	ND	ND	ND	>100	ND	ND	ND
95-50-1	1,2-Dichlorobenzene	ND	ND	ND	<20	ND	ND	ND	ND	ND	ND
106-46-7	1,4-Dichlorobenzene	<20	<20	ND	<20	ND	ND	ND	ND	ND	ND
67-72-1	Hexachloroethane	ND	ND	ND	49	ND	ND	ND	ND	ND	ND
91-20-3	Naphthalene	35	ND	ND	39	<20	ND	ND	ND	ND	ND
	ACID										
108-95-2	Phenol by GC/MS	71	58	1242	290	<50	ND	ND	ND	ND	ND
---	All acid extractables <50 ppb except 2,4 Dinitro-phenol and 4,6 Dinitro-cresol, <1000 ppb	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	METALS										
7440-36-0	Antimony	10	20	0.44	20	20	0.54	10	20	0.38	0.39
7440-38-2	Arsenic	28	20	0.76	56	10	0.26	9	<5	0.44	0.43
7440-41-7	Beryllium	<5	<5	0.020	<5	<5	0.020	<5	<5	<0.5	<0.5
7440-43-9	Cadmium	4.8	1.7	0.0998	7.8	4.1	0.67	1.2	1.3	0.945	0.149
7440-47-3	Chromium	42	28	5.79	24	42	25.8	14	16	42.5	39.0
7440-50-8	Copper	68	20	10.4	64	14	17.2	8	8	17.5	24.5
7439-92-1	Lead	100	30	21	250	50	150	<10	<10	44.5	18.5
7439-97-6	Mercury	1.7	<0.2	0.002	<0.2	<0.2	<0.002	<0.2	<0.2	0.31	0.07
7440-02-0	Nickel	50	<20	0.73	20	20	2.42	<20	<20	29.0	25.5
7782-49-2	Selenium	6	16	0.26	7	1	Undet.	<1	6	<0.1	<0.1
7440-22-4	Silver	21	27	0.30	10	6	1.12	28	<5	0.9	0.4
7440-28-0	Thallium	<50	<50	<0.05	<50	<50	<0.05	<50	<50	Undet.	Undet.
7440-66-6	Zinc	120	110	18.4	480	440	460	11	63	97.5	59.5
	PESTICIDES										
319-85-7	B-BHC	ND	ND	ND	ND	ND	ND	ND	ND	11	ND
58-89-9	g-BHC	ND	ND	619	ND	ND	ND	ND	ND	ND	<10
72-55-9	p,p'-DDE	19	ND	8077	ND	ND	ND	ND	ND	ND	ND
60-57-1	Dieldrin	ND	ND	1655	ND	13	ND	ND	ND	ND	10
959-98-8	Endosulfan, alpha	ND	ND	ND	ND	ND	48	22	ND	ND	ND
72-20-8	Endrin	ND	ND	44	ND	ND	ND	ND	ND	ND	ND
	MISCELLANEOUS										
	BOD_5 (mg/l)	190	40	X	156	20.3	X	2.4	5.9	X	X
	Chlorophyll A (mg/l)	<0.02	<0.02	X	0.073	<0.02	X	<0.02	<0.02	X	X
	COD (mg/l)	404	79.2	X	530	127	X	11.9	51.5	X	X
57-12-5	Cyanide (ug/l)	116	50	960	8	160	150	6	16	<1.46	<1.36
	Dissolved O_2 (mg/l)	4.0	>7.4	X	5	<10.5	X	11.8	11.8	X	X
	pH	7.1	6.7	7.2	9.3	6.9	6.8	7.2	6.9	7.1	7.0
Unknown	Phenolics, total (ug/l)	<20	20	<20	35	42.5	500	<20	20	<1.46	<1.36
	Settleable Solids (ml/l)	5.8	<0.1	X	2.4	0.2	X	<0.1	<0.1	X	X
	Suspended Solids (mg/l)	133	17.4	17,820	121	36	63,300	18.3	20	X	X
	Temperature (°C)	15	14.5	22	14	12.5	26	8.5	9.0	8.5	9.0
	TKN (mg/l)	23.5	13	390	20.5	16	1,150	1.2	2.1	1.35*	1.95*
	TOC (mg/l)	95.8	25.6	3700	124	61.2	13,500	22.6	29.9	X	X
	Total Phosphorus (mg/l)	5.6	1.6	430	9.8	3.4	1,600	<0.04	0.22	0.74*	0.59*
	Total Solids (mg/l)	446	301	10,000	576	396	64,100	62	104	68.6**	73.5**
	Turbidity (FTU)	68	14	X	78	23	X	23	22	X	X

(1) Units of ppb except ppm in sludges and sediments.

** Units of %

* Units of mg/g

X Not analyzed

ND Not Detected

UNDET. - Undetermined due to analytical interference

+ - Small sample may have produced spurious quantitation

A major difference in effluent quality exists between the plants in the loading of volatile priority pollutants. This is suspected to be a result of the operation of the activated sludge process at Richmond which allows increased chance for evaporation or biodegradation.

To compare the overall impact each plant may have on its receiving stream, the table below takes the highest concentration compound in each category and provides a daily discharge.

Table 4.3-2

Daily Discharge of Selected Priority Pollutants
by Culpeper and Richmond POTWs

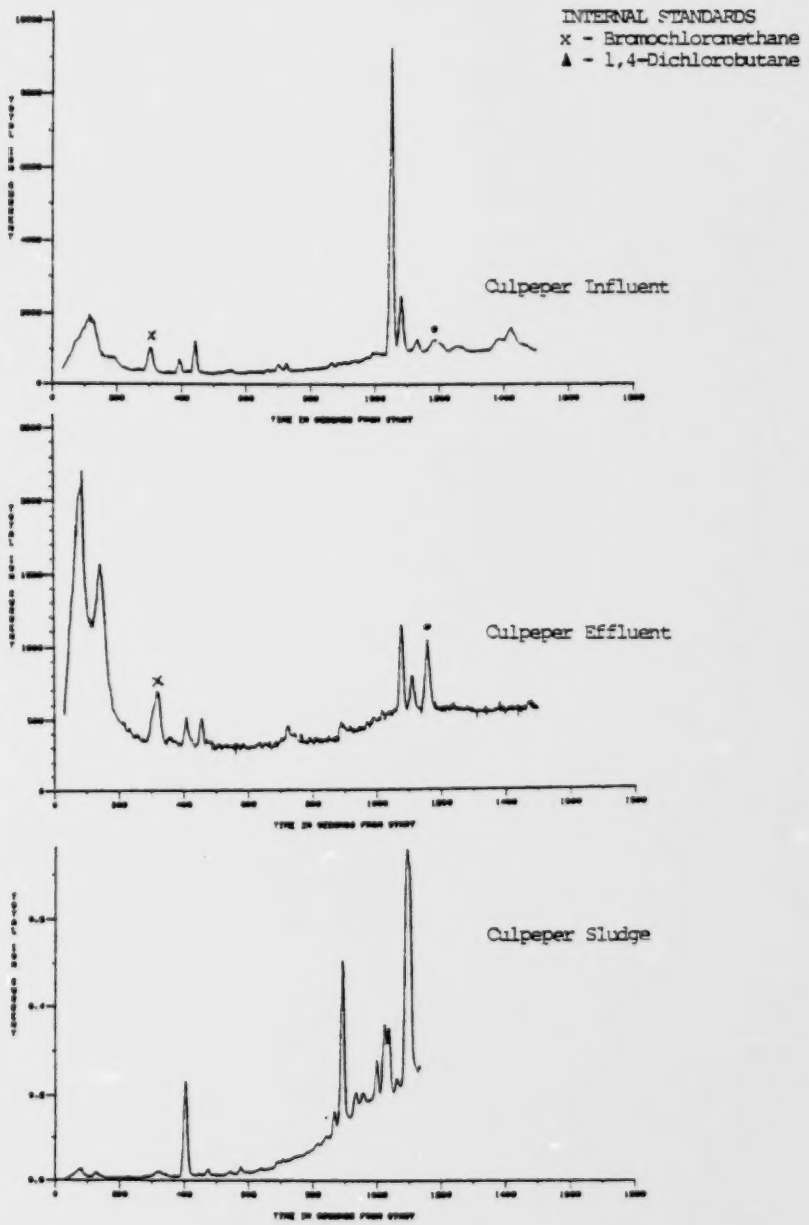
	CULPEPER (1.5 mgd)	RICHMOND (70 mgd)
PESTICIDES	dieldrin .0738 kg	ND
METALS	zinc 2.498 kg	zinc 31.535 kg
VOA	1,1,2,2-tetrachloroethylene 0.710 kg	methylene chloride 2.650 kg
ACID EXTRACTABLES	phenol 0.284 kg	phenol 13.250 kg
BASE NEUTRAL EXTRACTABLES	naphthalene 0.114 kg	bis(2-ethylhexyl)phthalate 24.115 kg
CYANIDE	cyanide 0.953 kg	cyanide 13.250 kg

4.3.1 Volatile Organics

Figures 4.3.1-1 through 4.3.1-3 provide total ion GC/MS chromatograms for the volatile organic analyses. In some cases, different vertical scales have been utilized. Ambiguities can be resolved by using the indicated internal standards as benchmarks.

Figure 4.3.1-1

Total Ion GC/MS Chromatograms for Culpeper
Influent, Effluent and Sludge Volatile Organics



Reproduced from
best available copy.

Figure 4.3.1-2

Total Ion GC/MS Chromatograms for Culpeper
Receiving Stream Water and Sediment Volatile Organics

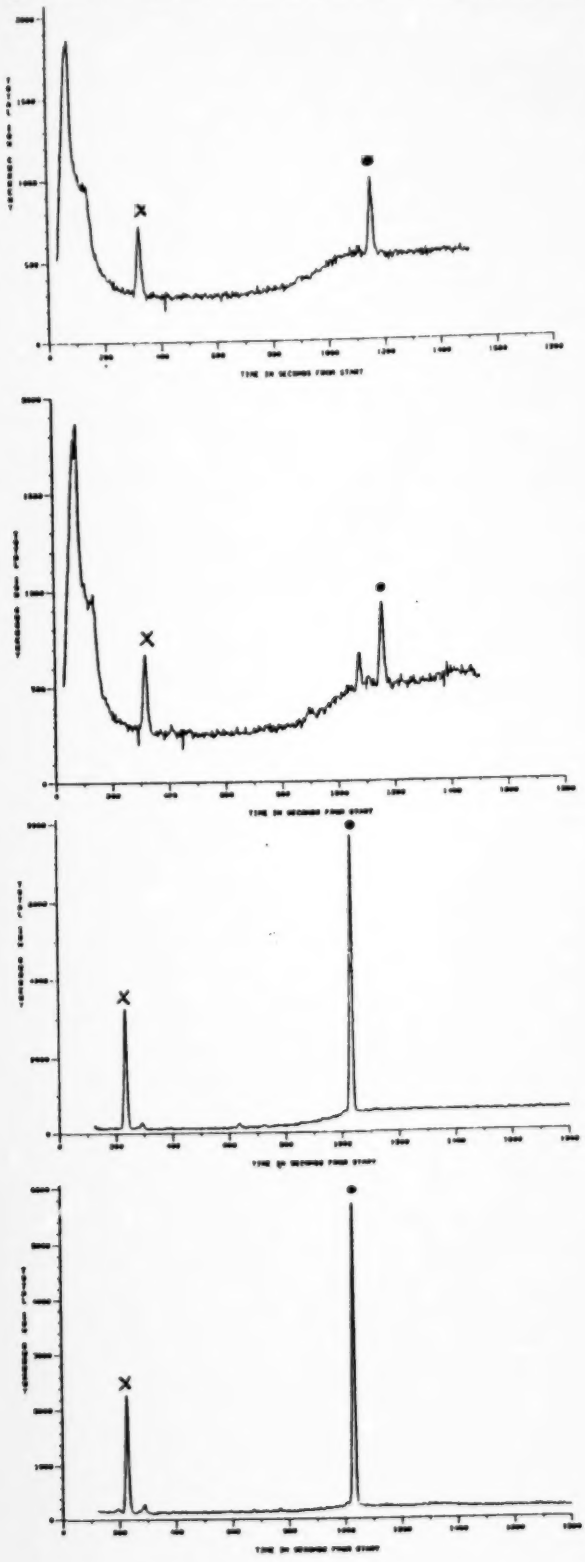
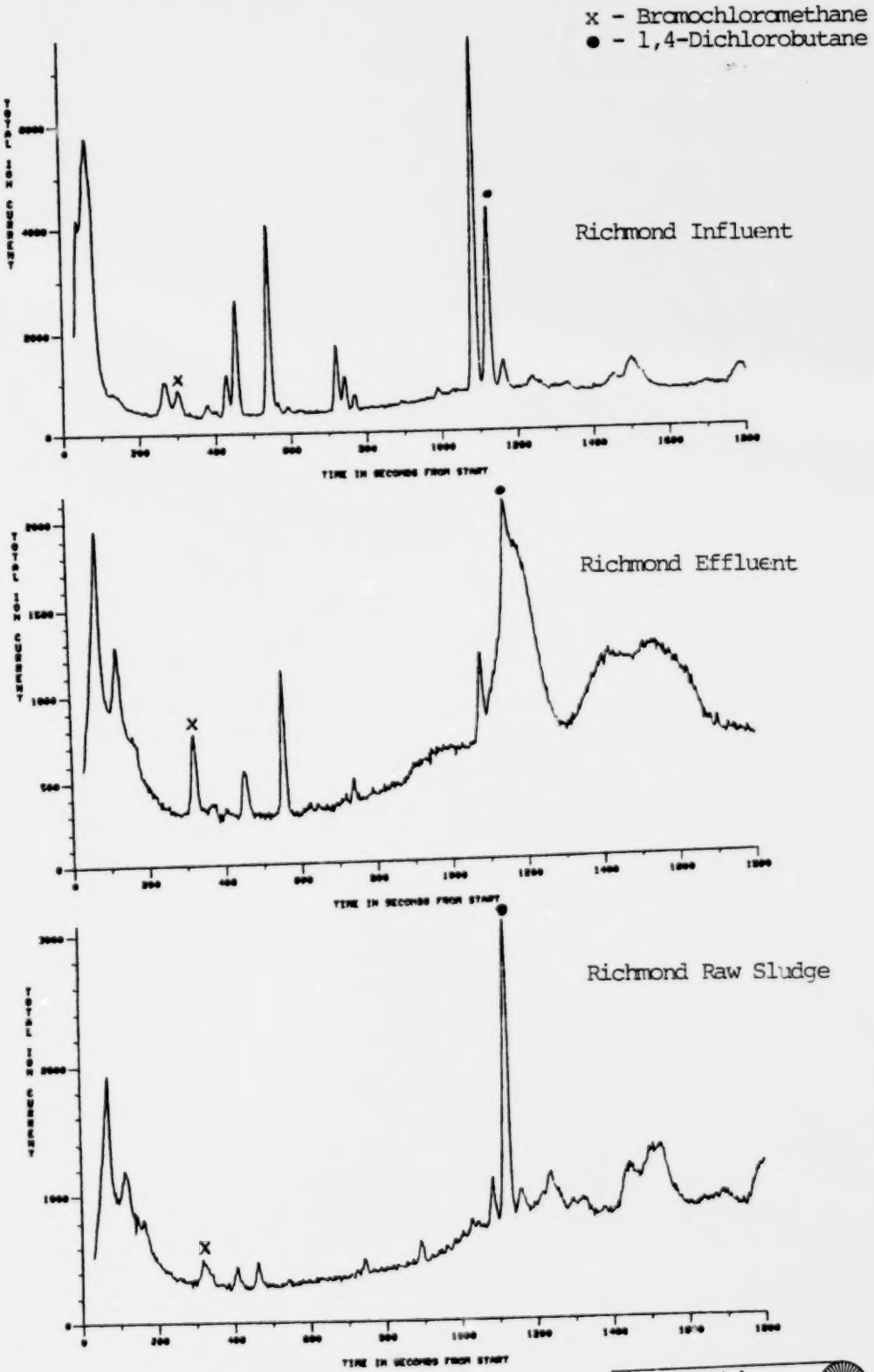


Figure 4.3.1-3

Total Ion GC/MS Chromatograms for Richmond Influent, Effluent and Sludge Volatile Organics



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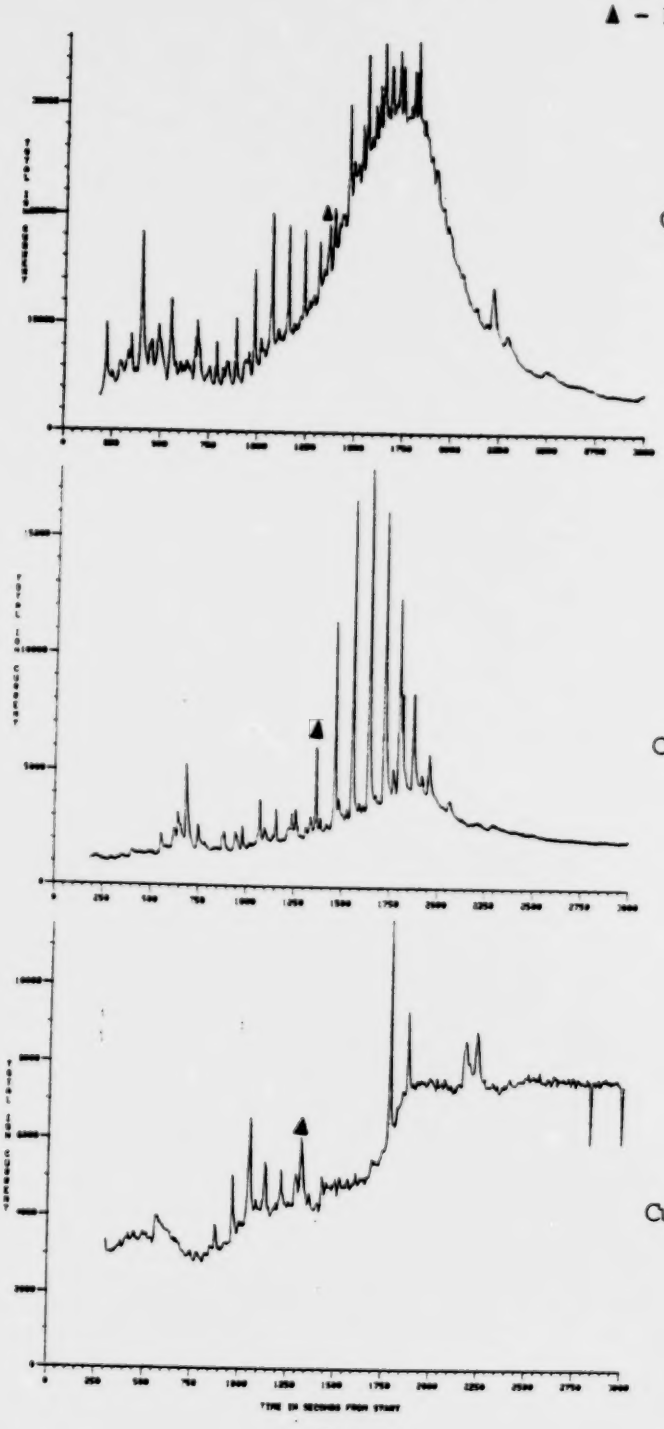
4.3.2 Base-Neutral Extractables

Figures 4.3.2-1 through 4.3.2-3 are total ion GC/MS chromatograms for the base-neutral extracts of the samples from both Culpeper and Richmond POTW's. The deuterated anthracene internal standard serves as a marker within each trace.

Figure 4.3.2-1

Total Ion GC/MS Chromatograms for Culpeper
Influent, Effluent and Sludge;Base/Neutral Fraction

▲ - Deuterated Anthracene



Culpeper Influent

Culpeper Effluent

Culpeper Sludge

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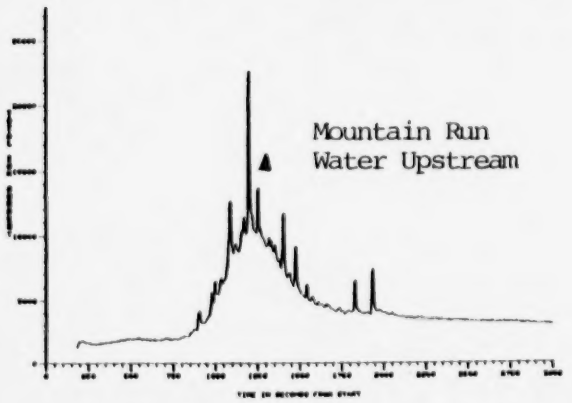
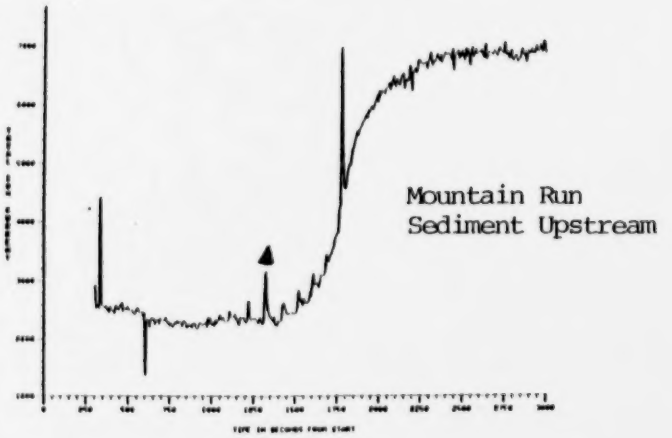
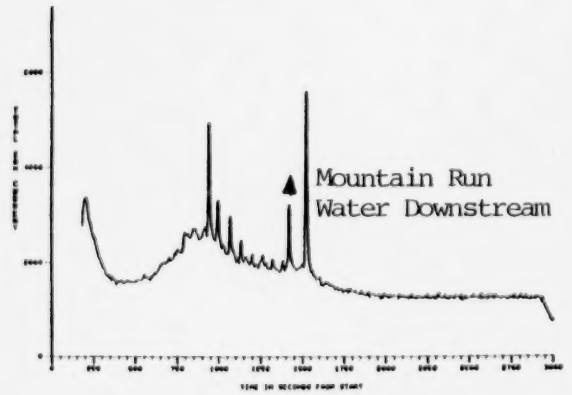
Figure 4.3.2-2

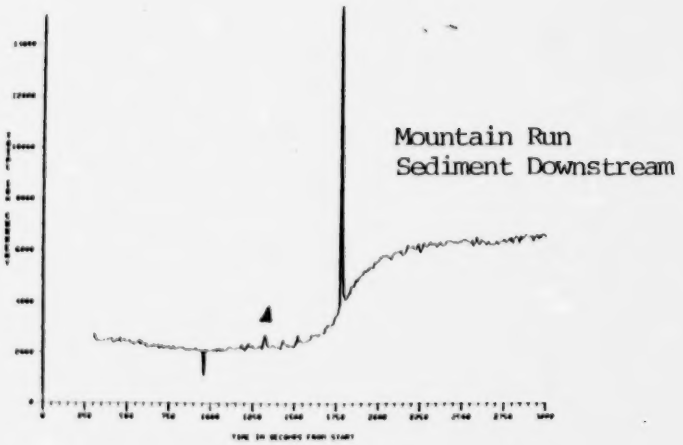
Total Ion GC/MS Chromatograms for Culpeper Receiving Stream
Water and Sediment; Base/Neutral Fraction

▲ - Deuterated Anthracene









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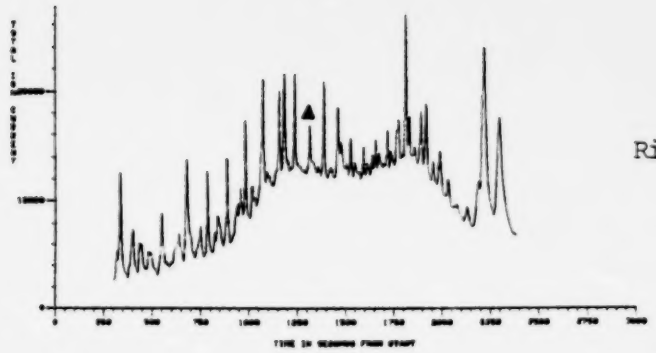
best available copy.

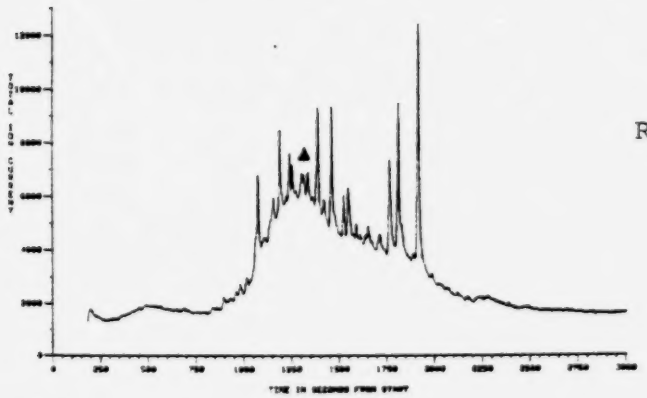
Figure 4.3.2-3

Total Ion GC/MS Chromatograms for Richmond
Influent, Effluent and Sludge; Base/Neutral Fraction

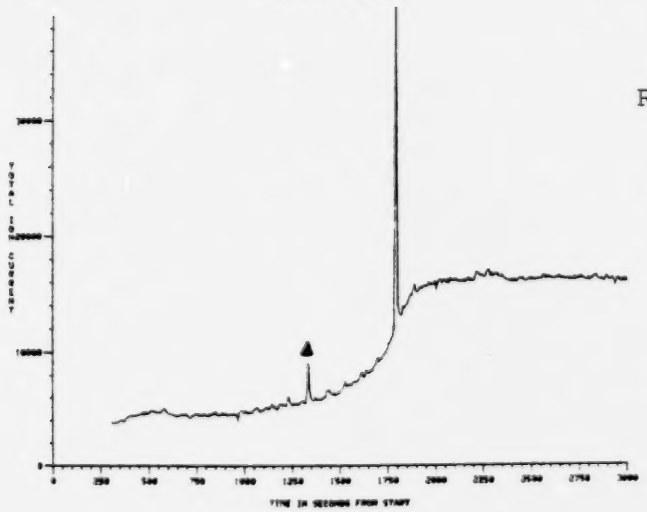
▲ - Deuterated Anthracene



Richmond Influent



Richmond Effluent



Richmond Raw Sludge

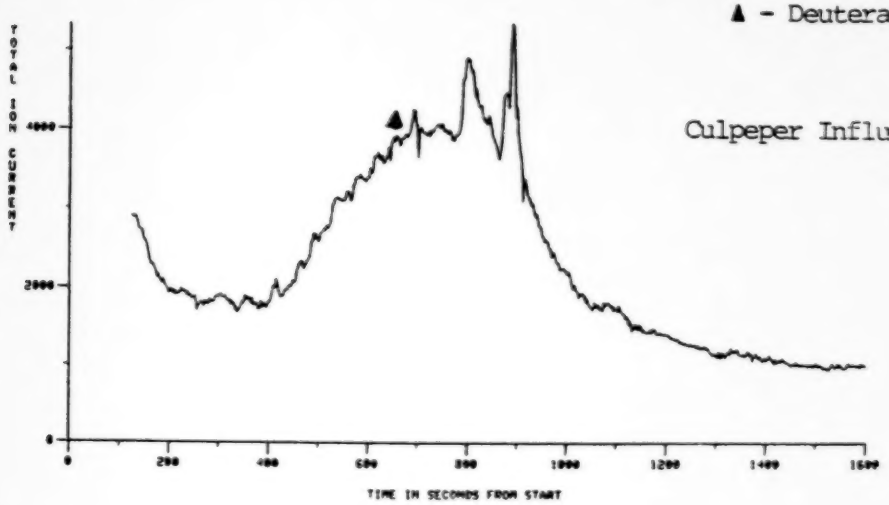
4.3.3 Acid Extractable Organics

Figures 4.3.3-1 to 4.3.3-3 provide total ion GC/MS chromatograms for the Culpeper and Richmond samples. Deuterated anthracene serves as internal standard through this series of traces.

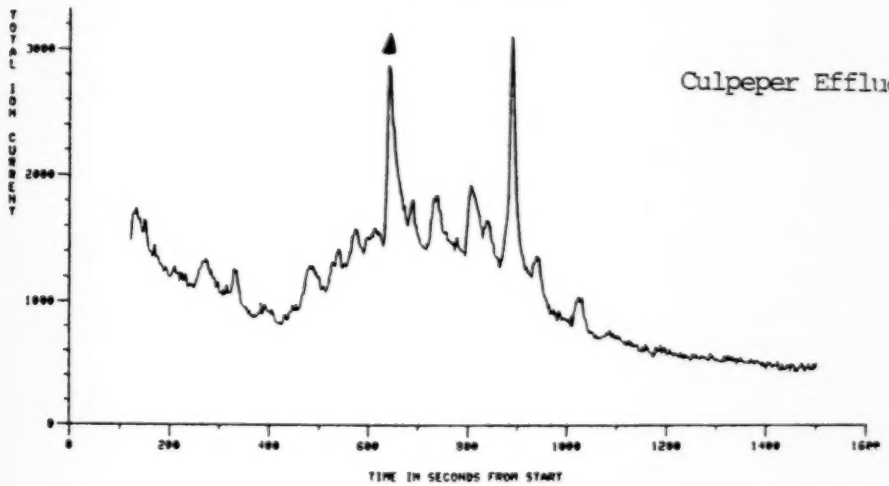
Figure 4.3.3-1

Total Ion GC/MS Chromatograms for Culpeper Influent, Effluent and Sludge; Acid Fraction

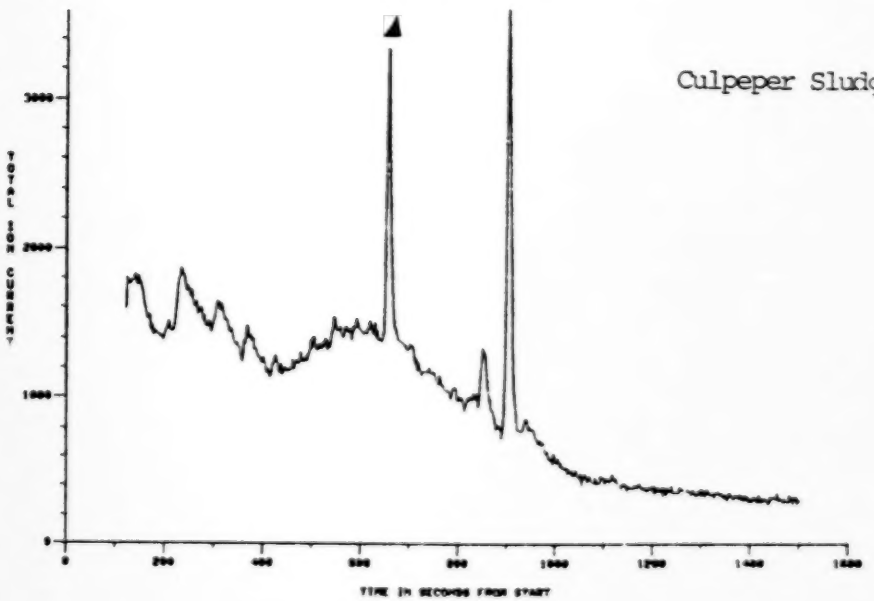
▲ - Deuterated Anthracene



Culpeper Influent



Culpeper Effluent



Culpeper Sludge

Figure 4.3.3-2

Total Ion GC/MS Chromatograms for Culpeper
Receiving Stream Water and Sediment; Acid Fraction

▲ - Deuterated Anthracene

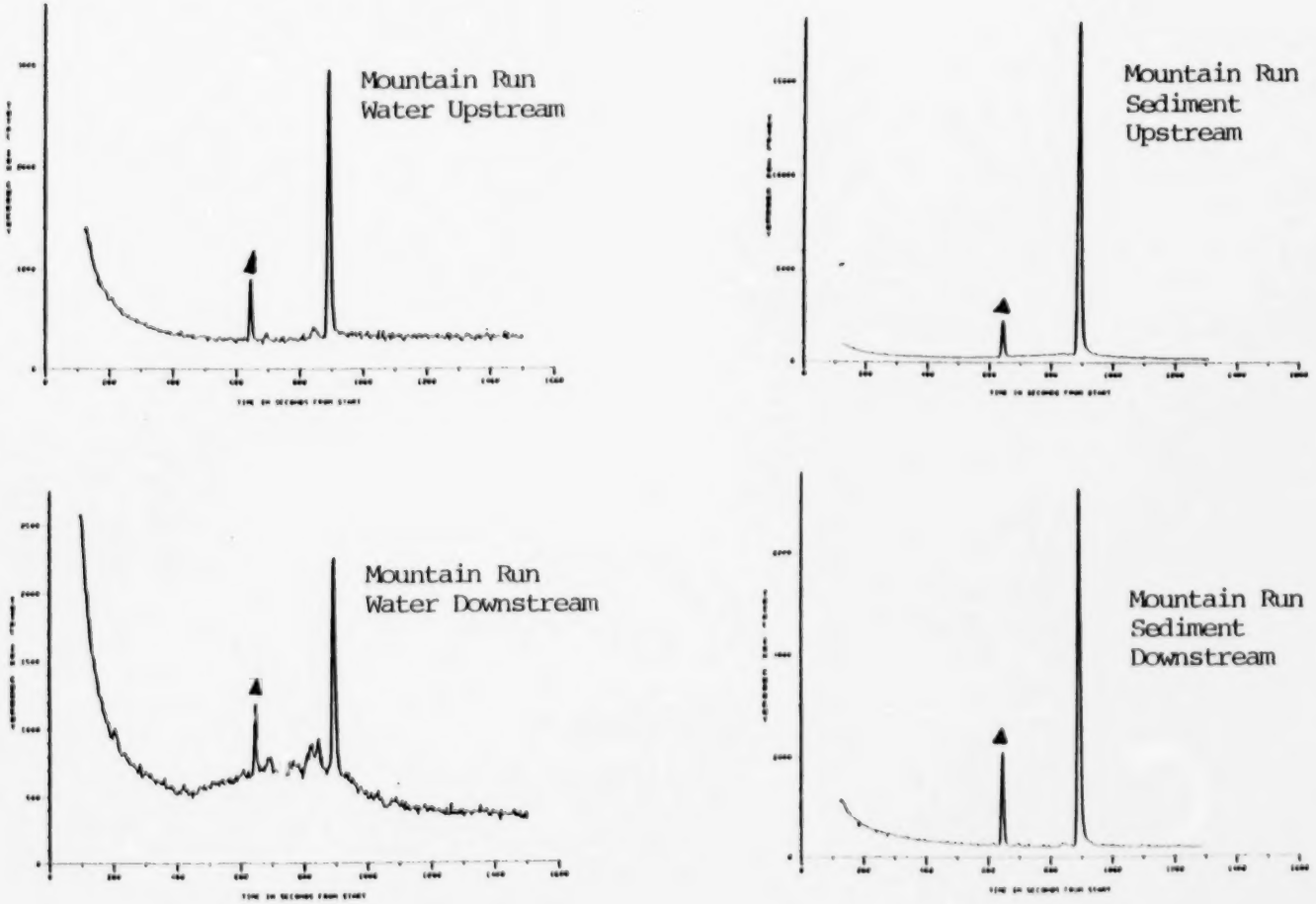


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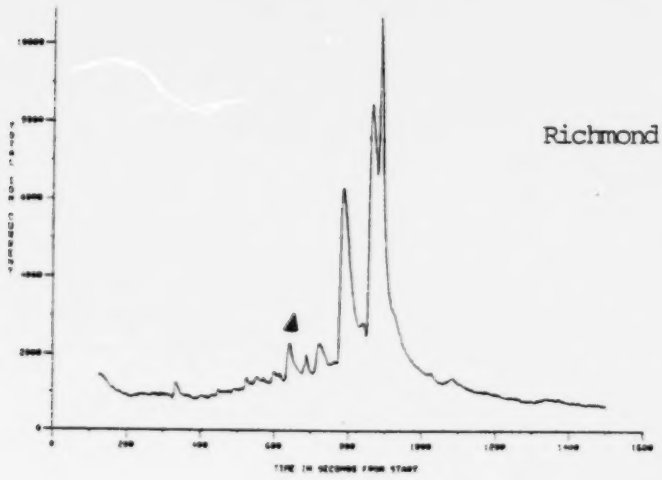
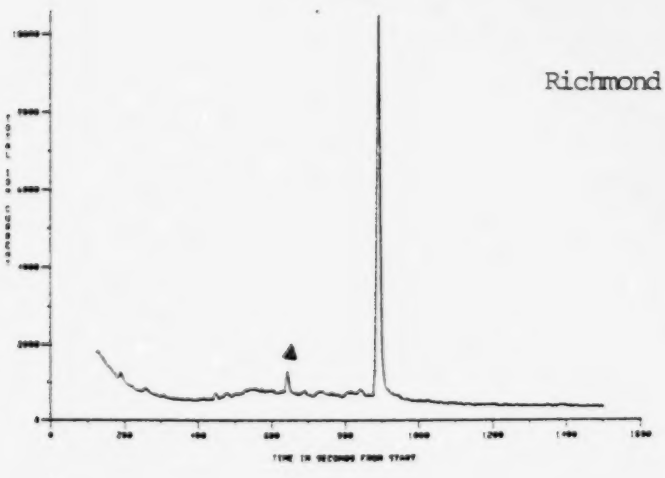
Figure 4.3.3-3

Total Ion GC/MS Chromatograms for Richmond Influent, Effluent and Sludge; Acid Fraction

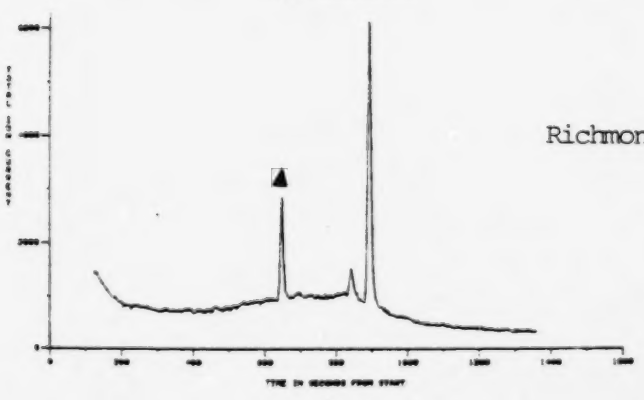
▲ - Deuterated Anthracene



Richmond Influent



Richmond Effluent



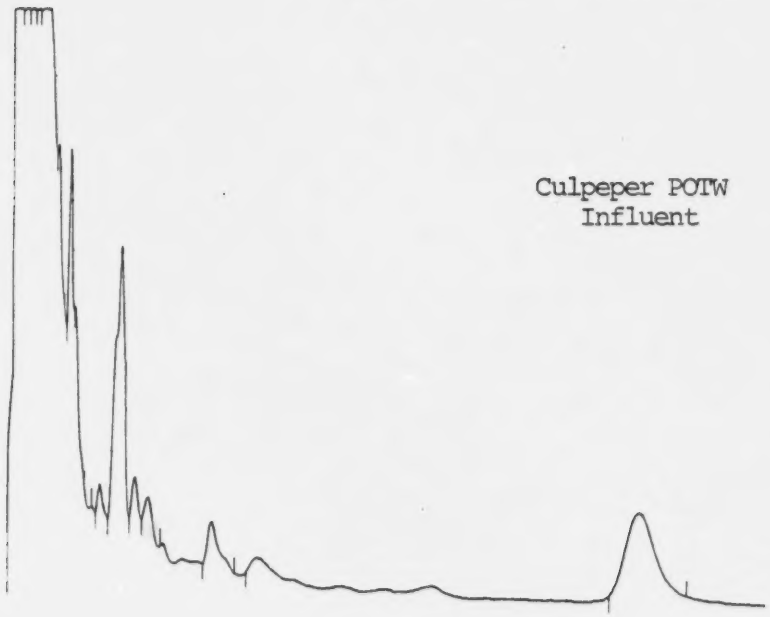
Richmond Raw Sludge

4.3.4 Pesticides

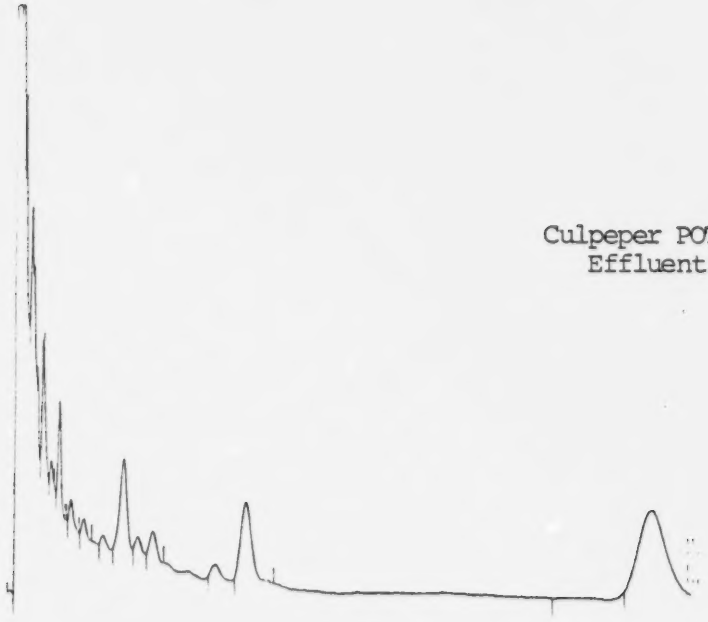
Pesticide chromatograms for the various samples are presented as Figures 4.3.4-1 to 4.3.4-6. Depending on the chemical complexity of the initial extracts they could be analyzed without further treatment. The Culpeper sludge sample (Figure 4.3.4-2) was sufficiently complicated to require separation into 3 separate fractions as shown.

Figure 4.3.4-1

Total Pesticide Chromatograms
Culpeper Influent and Effluent



Culpeper POTW
Influent



Culpeper POTW
Effluent

Figure 4.3.4-2

Pesticide Chromatograms from Culpeper Sludge

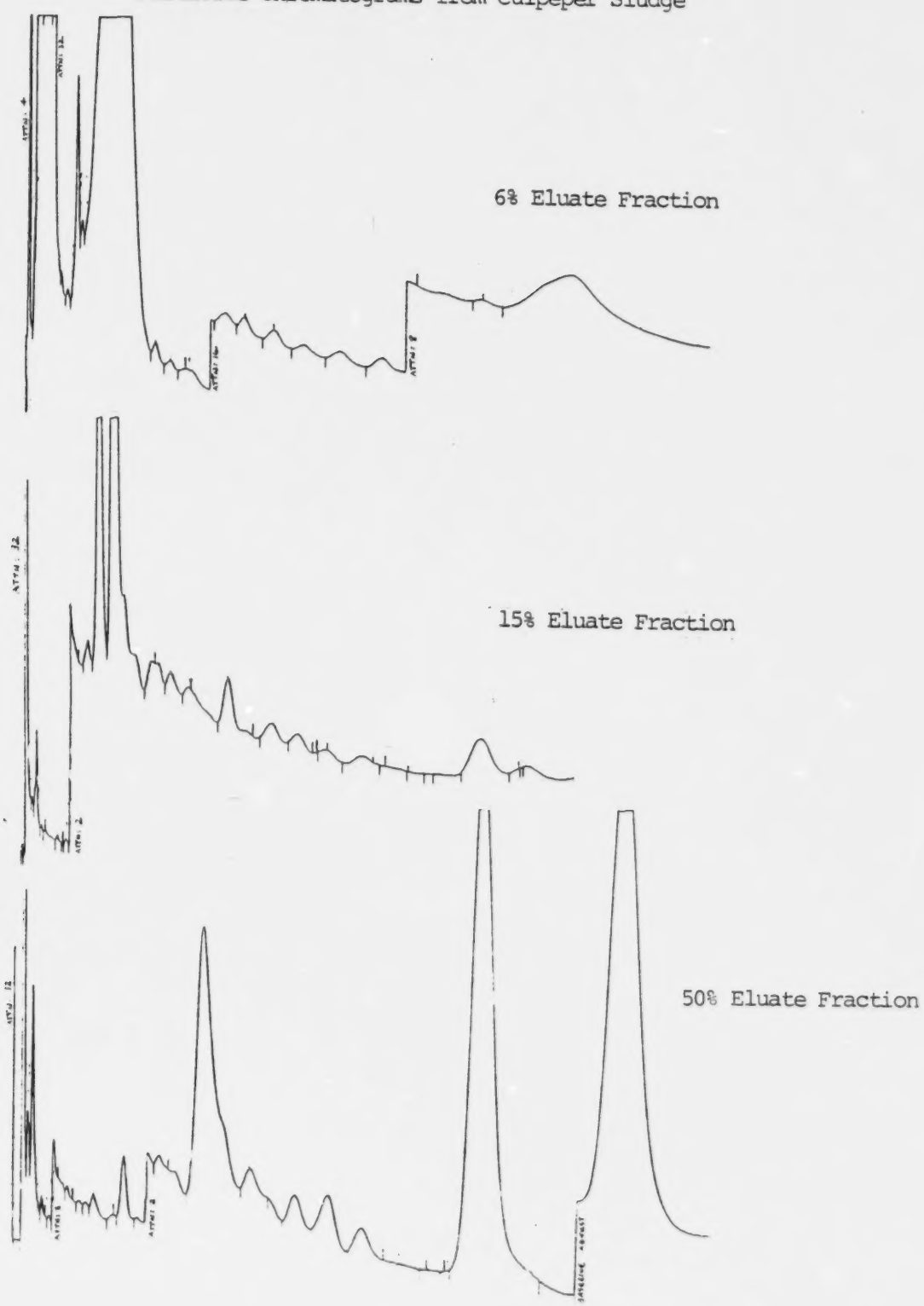


Figure 4.3.4-3

Total Pesticide Chromatograms
Culpeper Receiving Stream Water

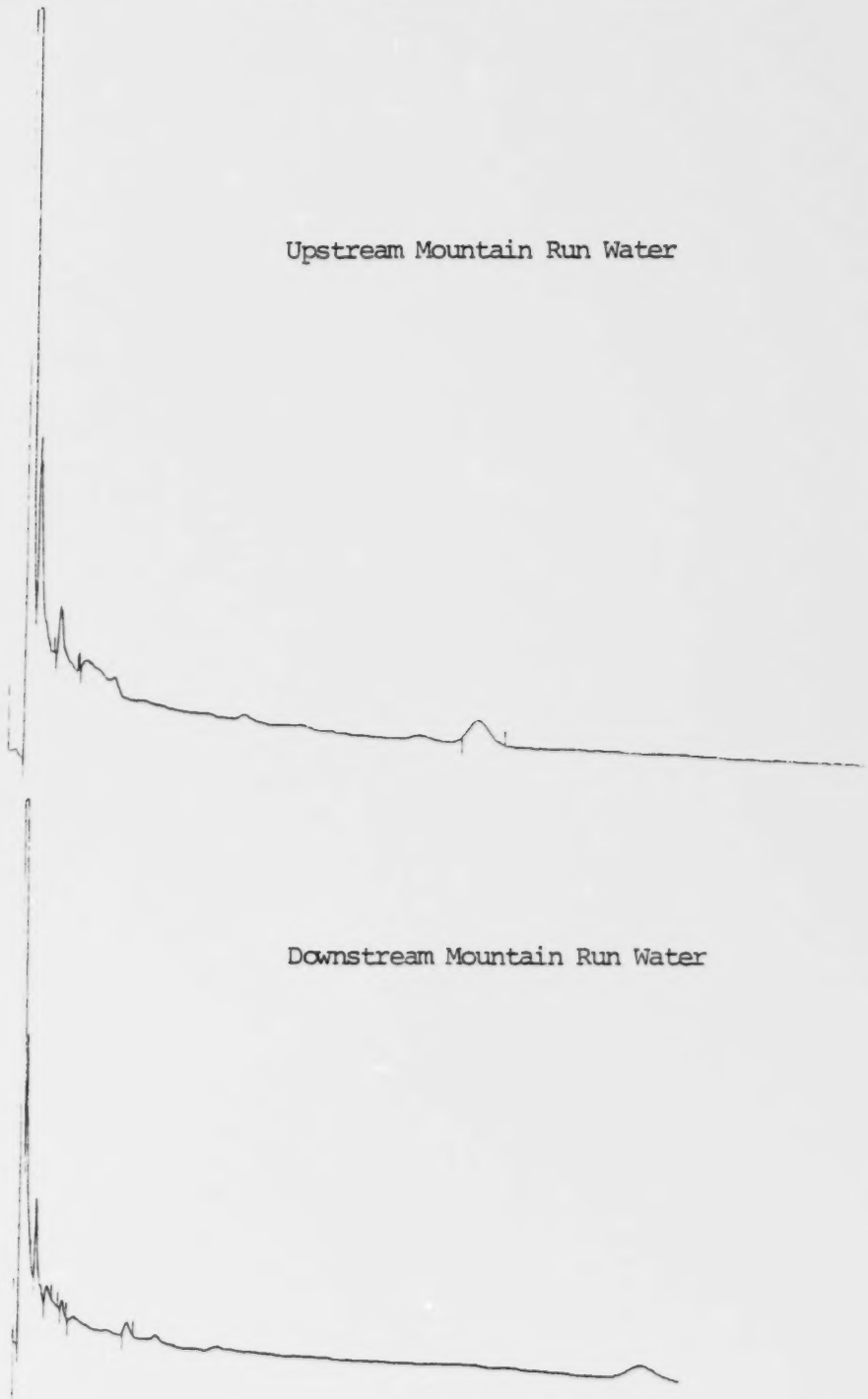


Figure 4.3.4-4

Total Pesticide Chromatograms
Culpeper Receiving Stream Sediment

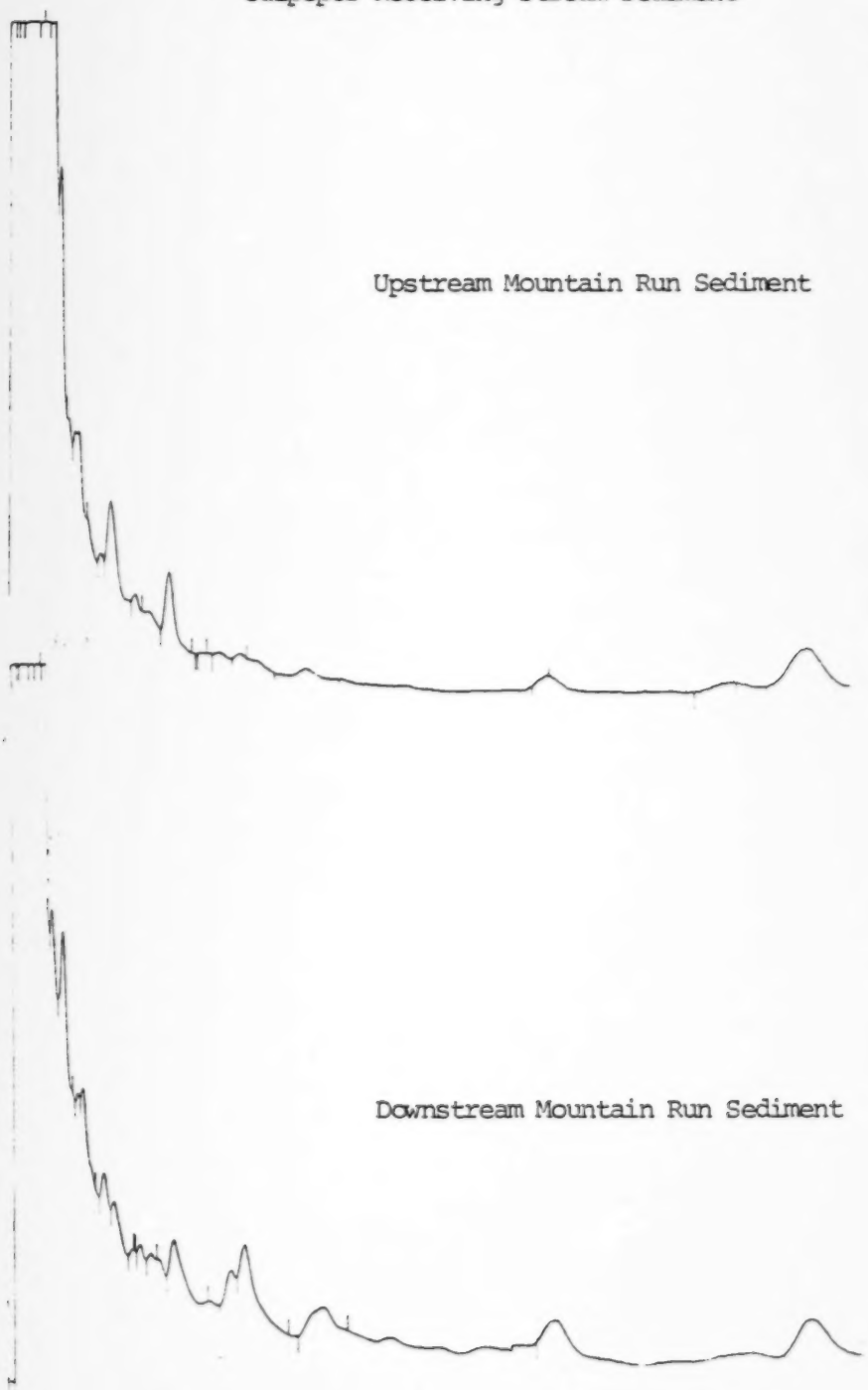
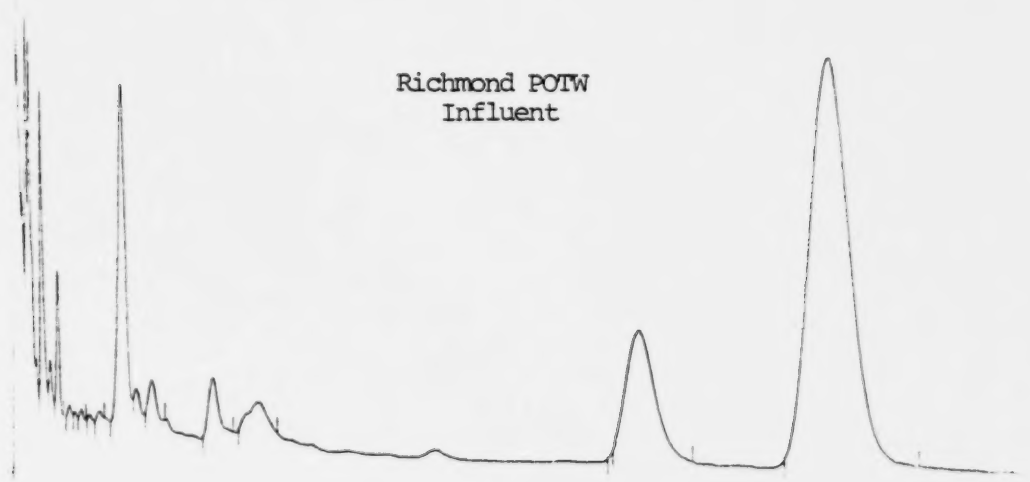


Figure 4.3.4-5

Total Pesticide Chromatograms
Richmond



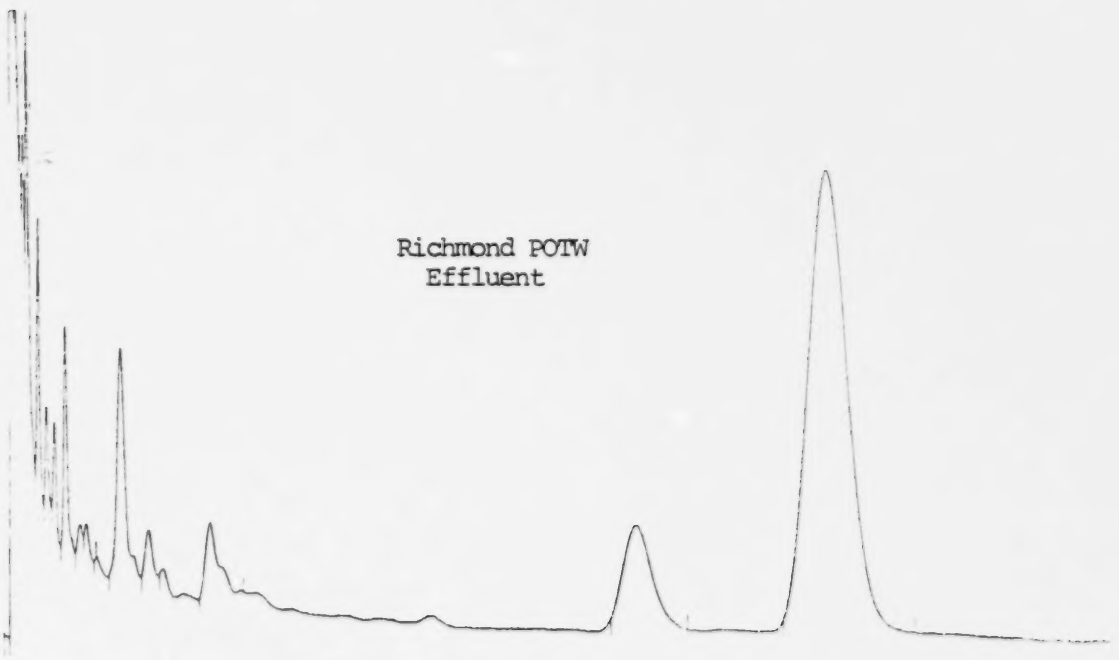
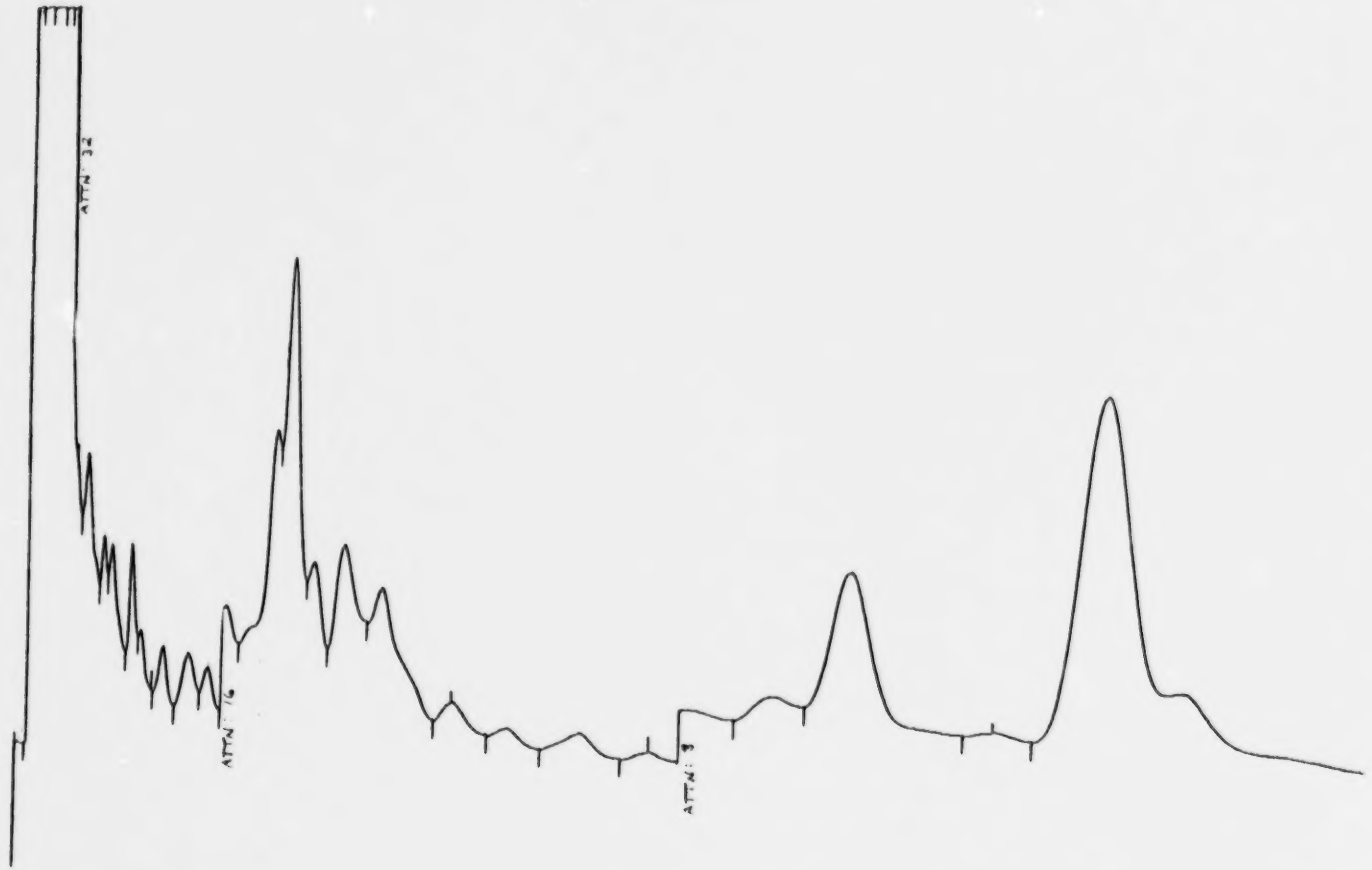


Figure 4.3.4-6

Total Pesticide Chromatogram
Richmond Sludge



5.0 REFERENCE

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2. Interim Methods for the Sampling and Analysis of Priority Pollutants in Sediments and Fish Tissue. USEPA, EMSL, Cincinnati, Ohio 45268. May 1978.

3. Weber, C.I. (ed.). 1973. Biological field and laboratory methods for measuring the quality of surface waters and effluents. EPA-670/4-73-001. Cincinnati, Ohio.

4. U.S. Environmental Protection Agency, Technology Transfer, Process Design Manual for Upgrading Existing Wastewater Treatment Plants, October, 1974.

5. U.S. Environmental Protection Agency, Office of Water Programs, Procedures for Evaluating Performance of Wastewater Treatment Plants (Contract 68-01-0107.)

6. U.S. Environmental Protection Agency, Criteria and Standards Division, PCBs Removal in Publicly-Owned Treatment Works, Final Report, Contract No. 68-01-3273, Task 13, April 19, 1977.

7. Herte, H. S., W.E. May, S.A. Wise and S.N. Chester. Trace Organic Analysis. Anal. Chem. Vol. 50, No. 4, April 1978, 429A.

A.1 VOLATILE ORGANIC ANALYSIS

An initial screening of the influent samples for VOA's was accomplished using gas chromatographic analysis with the flame ionization detector.

For analysis of volatile compounds the instrumental conditions were as follows:

Precolumn: 1' x 1/8" stainless steel

Packing: 3% carbowax 1500 on 60/80 mesh chromosorb WAW

Main Column: 8' x 1/8" stainless steel

Packing: 0.2% carbowax 1500 on 60/80 mesh chromosorb WAW

Temperature Program: Desorb 2 min. @ 30°C. Heat rapidly to 60°C and hold for 4 minutes. Program at 8°C/min. to 160°C and hold for 16 minutes.

Carrier Gas: N_2 at 25 ml/min

Inlet Temperature: Ambient

Detector Temperature: 250°C

Attenuation: Range 10, attn. 2

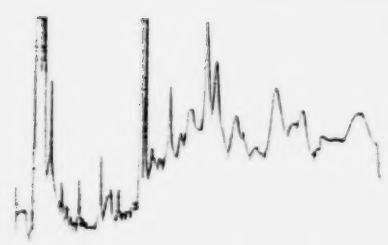
Tenax Trap on Tekmar Concentrator baked between runs for 20 min. @ 270°C.

Volatile compounds were identified by matching their retention times against standard compounds presented to the chromatographic column. The goal of the analysis was to provide data for a relative comparison of the eight plants. Therefore, an inordinate amount of effort was not made to identify each chromatographic peak. A selection of volatile standards was utilized that were suspected in significant concentrations for the purposes of calibration.

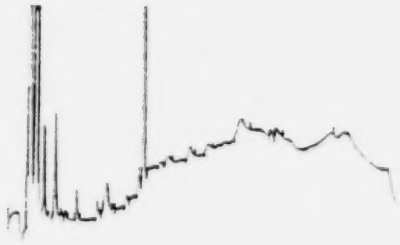
Figure A.1-1 shows the GC/FID chromatograms for each influent sample.

FIGURE A.1-1

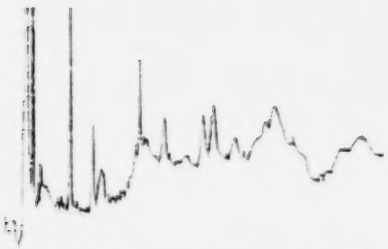
GC/FID VOA ANALYSIS CHROMATOGRAMS FOR INFLUENT SCREENING SAMPLES



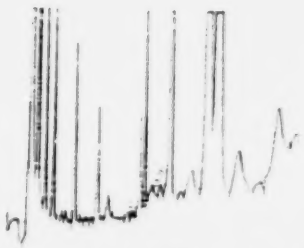
Culpeper



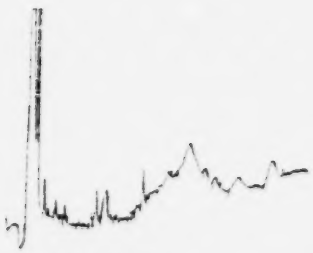
Lynchburg



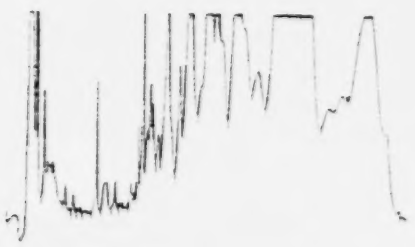
Charlottesville - Meadow's Creek



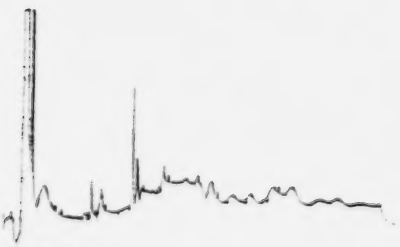
Charlottesville - Moore's Creek



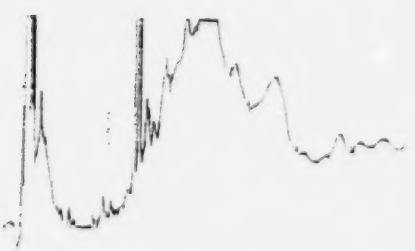
Harrisonburg



Waynesboro



Roancke



Staunton

The Richmond and Culpeper influent streams showed essentially the same list of compounds with only 3 exceptions. The compounds are common solvents.

chloroform
1,1,1-trichloroethane
trichloroethylene
1,1,2,2-tetrachloroethylene
benzene
ethyl benzene
toluene

In addition, Culpeper carried dichlorobromomethane. Methylene chloride and trans-1,2-dichloroethylene were observed at Richmond.

In the effluent streams of both facilities large reductions in concentration were observed, being the greatest at Richmond.

A comparison of the sludges shows significant concentrations in the Culpeper sludge with 390 ppb toluene noted. At Richmond concentrations are significantly lower. For such compounds this may be a result of the opportunity presented for volatilization during passage through the aeration basin in the activated sludge treatment process.

One also observes a number of compounds in the sludge not reported in the influent. Possible explanations include, low concentration input below detection limit, irregular input, process chemical input, and so on.

Very little inference can be made on the impact of the volatiles in the downstream environment. This is due to poor detection limits for the head-space VOA technique. The detection limits reported are those for which recovery of a spike could be easily quantitated. No data is available on the fate of a volatile organic added to a sediment slurry. We only know that if we spike enough, eventually some will appear in measurable quantities in the head-space.

Detection limits were taken to be the amount which was spiked and yielded a proper, 3 characteristic ion, GC/MS response. That amount was then apportioned over the weight of sample to yield a concentration as a detection limit.

Further exploration might allow a lowering of these detection limits as the chemistry of the system was better understood. Since no reference materials are available for volatile organic compounds, QC efforts centered on measurements of precision. A series of measurements were made on aliquots separately encapsulated in the field.

Table A.1-2 shows the results of these analyses. The data for each of 3 determinations was combined to yield a mean value and the average deviation from that mean expressed as a percent of the mean. The raw data was normalized to an internal standard to eliminate instrumental sensitivity changes as a bias. In all four compounds, all normalized data fitted within a ± 25% band about the mean. Consideration of the small number of data points limits more rigorous statistical treatment.

Table A.1-2

Precision of VOA Analysis on Replicate Influent Samples

Compound	Mean Value* (ppb)	Av. % Dev.
Chloroform	10.9	11.3
Toluene	12.9	8.9
Trans-1,2 dichloroethylene	11.9	9.0
Trichloroethylene	4.0	9.0

*Average of 3 determinations

A.2 BASE-NEUTRAL EXTRACTABLES

A screening for the compounds in the base-neutral fraction of the influent screening samples was accomplished using the GC/FID detection system.

Column: 6' x 4 mm ID glass column packed with 1% SP-2250 on 100/120 mesh Supelcoport

Flow Rate: 35 ml/min N_2

Column Temperature: 110°C for 4 minutes, program 8°C/min rise to 260°C and hold for 16 min.

Injection Port Temperature: 250°C

Detector Temperature: 250°C

Attenuation: Range 10, atten. 2-16

1 liter of sample was adjusted to pH greater than 12 and extracted with 450 ml total of methylene chloride. Sample was concentrated to 1 ml in methylene chloride and 2 µl injected into GC.

The two largest identifiable constituents were dimethyl phthalate at 2.8 ppm, and pyrene at 0.32 ppm. One does observe later eluting peaks of significant height and width. Future study might be profitably directed toward the identification and quantitation of these compounds.

Table A.2-1 gives the results of the GC/FID screening of the influent samples for base-neutral extractable semi-volatile organics. Since the goal was an analysis for comparison, extensive quantitation was not employed.

Figure A.2-1 presents the GC/FID chromatograms. The processes responsible for the elevated baselines have not been identified.

The base-neutral extracts of the effluents were subsequently analyzed by GC/MS after 90 days storage under protocol conditions of closure and temperature. Table A.2-2 shows these results, while total ion chromatograms appear in Figure A.2-2.

No published data has been found that corroborates the stability and chemical integrity of such stored extracts.

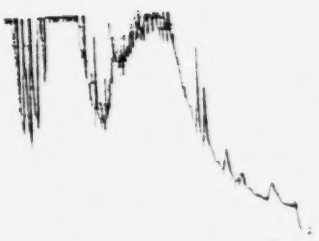
Table A.2-1

Influent Base-Neutral Extract Compound Summary

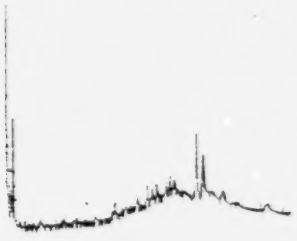
Staunton	Dimethyl phthalate (DMP) @ 40 ppb Low local peaks, most < 10 ppb
Harrisonburg	High concentration of early peaks. Otherwise very clean. < 40 ppb
Culpeper	DMP @ 2,800 ppb. Pyrene @ 320 ppb. Even distribution of large peaks - unidentified, concentration of 100 ppb
Lynchburg	Very clean. Perhaps 200 ppb trichloro-benzene. Peaks < 5 ppb.
Roanoke	Evenly distributed low peaks. Some low boilers, less than 25 ppb
Charlottesville - Meadow Creek	Highest unidentified phthalates, about 200 ppb. Other perhaps < 10 ppb
Waynesboro	DMP @ 1,000 ppb. High concentration of low boilers, perhaps DCB @ 1,600 ppb. Best defined peaks. Low peaks < 15 ppb.
Charlottesville - Moore's Creek	Di-n-butylphthalate @ 260 ppb. Defined peaks, most < 10 ppb.

FIGURE A.2-1

GC/FID BASE NEUTRAL ANALYSIS CHROMATOGRAMS
FOR INFLUENT SCREENING SAMPLES



Culpeper



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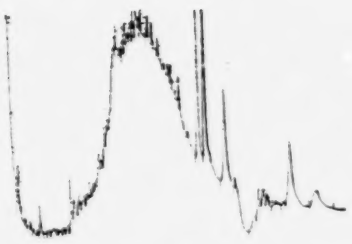
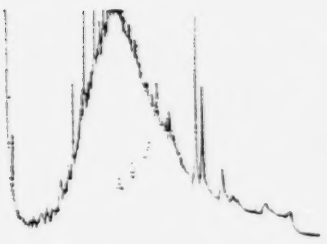
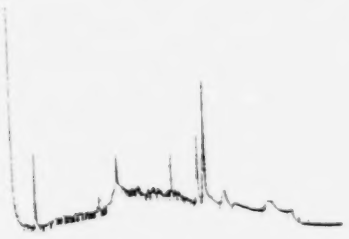


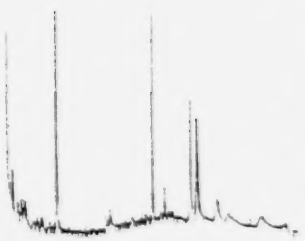
Charlottesville - Meadow's Creek



Charlottesville - Moore's Creek



Harrisonburg



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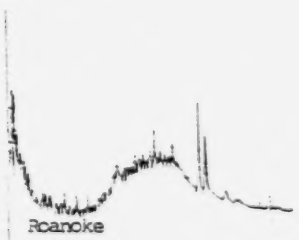
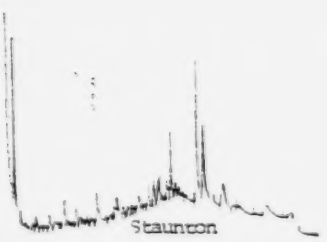


Roanoke



Staunton

Table A.2-2

Influent Base-Neutral Concentrations by GC/MS**

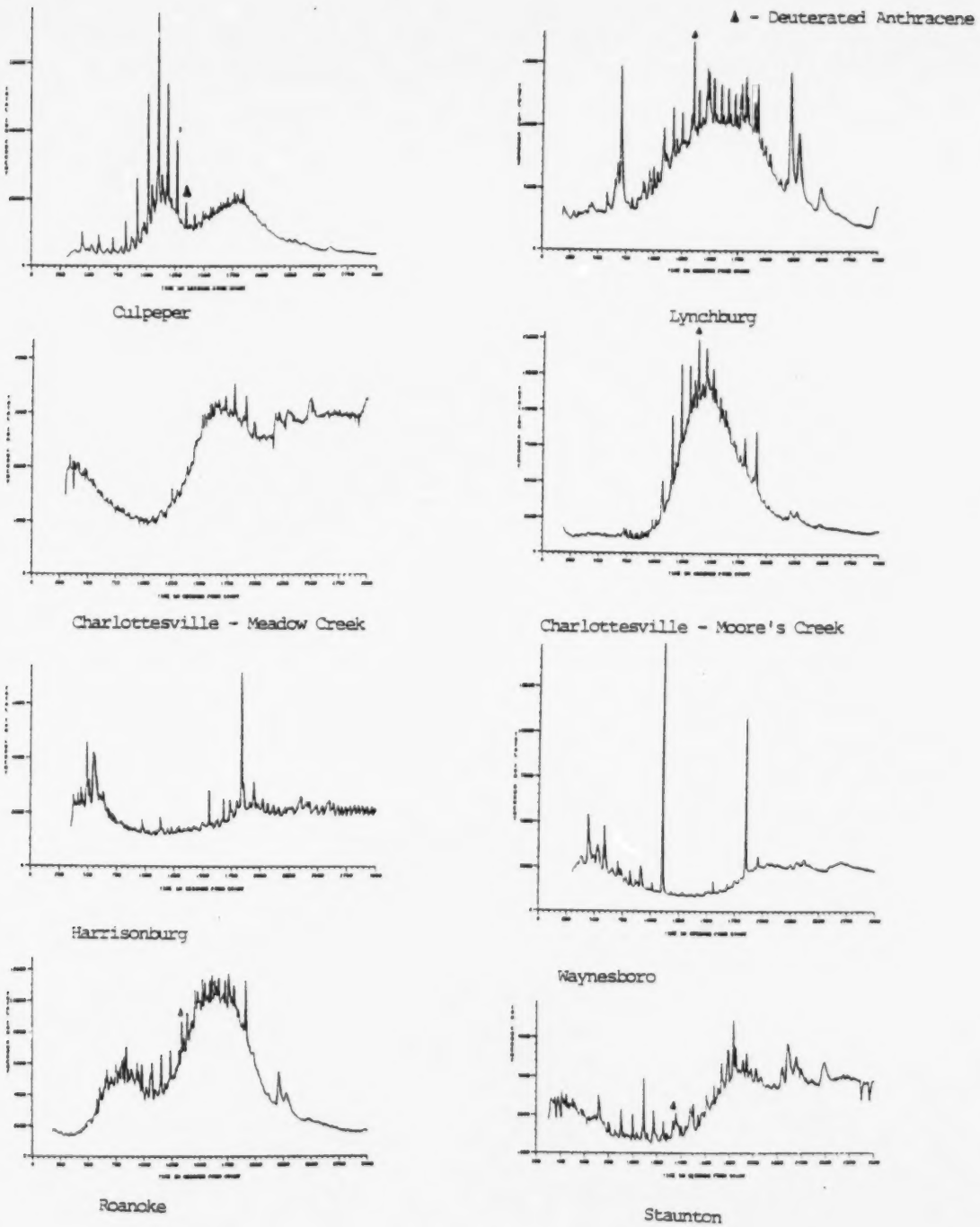
	Naphthalene*	bis(2-ethylhexyl)phthalate*	di-n-butyl phthalate*
Charlottesville-Meadow Creek	ND	67	< 20
Moore's Creek	ND	< 20	ND
Culpeper	< 20	ND	ND
Harrisonburg	ND	>100	ND
Lynchburg	< 20	ND	ND
Roanoke	ND	< 20	< 20
Staunton	ND	20	< 20
Waynesboro	< 20	>100	ND

*All ppb.

**Analyzed by GC/MS after 90 day extract storage.

Figure A.2-2

Total Ion GC/MS Chromatograms for Influent Screening Samples - Base/Neutral Fraction



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A.3 ACID EXTRACTABLES

In both plants the only acid extract compound found was phenol. Of interest is a comparison of that data with the 4AAP method for total phenolics as outlined in Methods of Chemical Analysis for Water and Waste Water (EPA). In the priority pollutant protocol the sample is stored in glass at 4°C without preservative. The 4AAP method specifies $CuSO_4$ and phosphoric acid to pH = 4 as preservatives. Figure A.3-1 provides GC/MS total ion chromatograms for the acid extractable fraction of the influent screening samples.

The priority pollutant protocol measures phenol by GC/MS after an acid extraction. The analysis provides data on 11 specific phenol compounds. The 4AAP is a colorimetric procedure which gives a low value for phenol since para-substituted phenols do not form the colored complex required for analysis.

In the absence of further information a direct interpretation of the data for the Culpeper influent by the two methods is not possible except to say that different species are obviously contributing to the analysis.

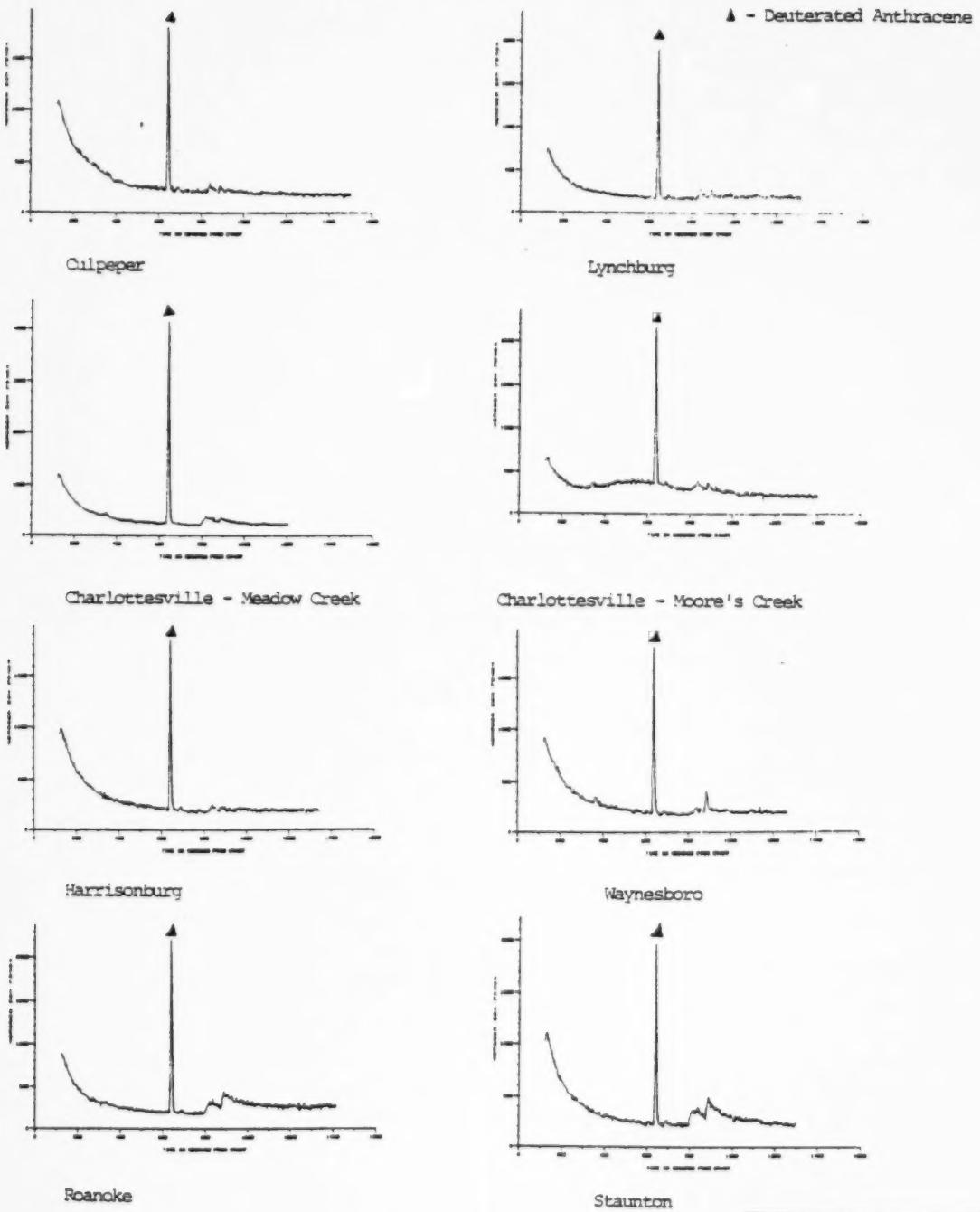
Culpeper Influent	
Phenol by GC/MS of Acid Extract	290 ppb
Total Phenolics by 4AAP Method	35 ppb

A 1000 ppb detection limit for 2,4 dinitrophenol and 4,6 dinitro-o-cresol could allow a good deal of undetected chemical which might bias results.

Work in the EPA Region VII lab reported at the Denver, Nov. 1977 meeting has shown protocol procedures to provide % recovery of spikes to fall in the range of 30% to 61% which further complicates any interpretation at this time.

Dr. Bob Kloepfer of EPA Region VII laboratory reported at the May 1978 Savannah Priority Pollutant Protocol Symposium that acid-extractable semi-volatiles spiked at 200 ppb into distilled water were recoverable at an average of 52% ± 1σ of 14%. No recovery data is published for environmental matrices.

Figure A.3-1
Total Ion GC/MS Chromatograms for Influent Screening Samples - Acid Fraction



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A.4 TOTAL PHENOLICS

Total phenolics (i.e., ortho and meta substituted phenols) are determined by the standard EPA procedure in 1974 Methods of Chemical Analysis of Water and Wastewater with the assistance of a Technicon Auto Analyzer. The method is based on the distillation of phenol and the subsequent reaction of the distillate with alkaline ferricyanide and 4-aminoantipyrine to form a red complex which is measured colorimetrically at 505 nm. The data in this report was generated by application of the automated procedure used with the Technicon Auto-Analyzer.

Table A.4-1 shows the values for total phenolics in the POTW influent screening samples.

Table A.4-1

Total Phenolics in POTW Influent Screening Samples

Sample	Amount Found (ppb)
Charlottesville, Meadow Creek	110
Culpeper	95
Charlottesville, Moore's Creek	90
Staunton	85
Waynesboro	75
Roanoke	55
Lynchburg	45
Harrisonburg	30

In both Culpeper and Richmond there are apparent processes which lead to higher phenol concentrations in effluents than in the corresponding influents. There is a build-up in the Culpeper sludge, which is not the case at Richmond.

QC efforts for total phenolics are presented in Table A.4-2. The precision of this method is acceptable but improvement is possible.

Table A.4-2

Total Phenolics in QC Samples

QC#	Added (ppb)	Found (ppb)	Δ	% Diff.
107	200	217.5	+17.5	+ 8.7
108	98.95	110	+11.05	11.2
109	520	495	-25	- 4.8
110	52	45.0	- 7	- 13.5
111	104	105	+ 1	- 0.9
112	Blank	<20	---	---

A.5 CYANIDE

Cyanides in the influent streams were analyzed using the EPA procedure in "Methods of Analysis for Water and Wastewater" 1974. This consists of releasing the cyanide as hydrocyanic acid (HCN) by refluxdistillation, then absorbing the HCN in a sodium hydroxide scrubber. The cyanide ion in the scrubber solution is determined colorimetrically by conversion to cyanogen chloride by reaction with chloramine T at a pH less than 8. Color formation is by addition of pyridine-pyrazolone or pyridine-barbituric acid reagent. The data in this report was generated by application of the automated procedure used with the Technicon Auto-Analyser.

Table A.5-1

Cyanide in POTW Influent Screening Samples

	Amount Found (ppb)
Lynchburg	110
Charlottesville, Moore's Creek	22
Charlottesville, Meadow Creek	10
Harrisonburg	8
Culpeper	5
Roanoke	5
Waynesboro	5
Staunton	5

The cyanide shows concentration in the sludge at both Culpeper and Richmond. A major surprise is the apparent production of CN within the Culpeper plant. An influent/effluent ratio of 8/168 was observed. It is corroborated by recalling a ratio of 12/60 in the data from the first visit. No immediate cause for this finding is apparent. However, prior experience in sampling POTWs has shown that long before any exotic chemical transformation must be hypothesized, a careful assessment of the total piping system must be carried out. The possibility of extra influent lines or periodic acceptance of septic tank pumpouts are the kind of things which are often hidden from an initial inspection. It is not clear why the chlorine treatment has not reduced the cyanide to a lower value.

Table A.5-2 shows the results of blind QC samples submitted to the laboratory concurrent with the analysis of the POTW samples. These results compare favorably with long term assessment of the cyanide analysis applied to environmental samples.

Table A.5-2

Cyanide QC Results

Lab No.	QC No.	Added(ppb)	Found(ppb)	Δ	% Diff.
2671	97	200.8	199	-1.8	0.89
2672	98	Blank	< 5	--	--
2673	99	99.3	100	+0.7	0.7
2674	100	19.9	22	+2.1	+10.5
2675	101	9.89	11	+1.11	+11.2

A.6 METALS

Metals found in the screening samples are tabulated in Table A.6-1. Two different sites were sampled at Harrisonburg. Notice that Zn varies by a factor of 2 and Ag by 2.4 while others such as Pb are constant.

Zinc is seen to be the most concentrated of the metals ranging from 60 to 540 µg/l. Little beryllium or thallium was seen.

Metals in Culpeper and Richmond

Measurable quantities of all metals except thallium were found in the two plants. An overall tendency is for an apparent enrichment in the sludge phase with a 150 ppm lead concentration reported for Culpeper.

The metal values for the Culpeper receiving stream sediments do not show a consistent picture of deposition downstream. Without a better accounting of the variability found in the sediment analyses as a function of location it is risky to hypothesize. There may be a net pH decrease in the reach below the outfall which might promote some leaching of surficial sediments. The sediment itself is very cohesive and quite coarse as a result of the relatively high speed of Mountain Run.

The metals data show the generalized pattern of enrichment in the solid phases as has been previously observed and reported.

Metals QC Efforts

Metal QC data is a result of both in-house spiking of samples as well as analysis of EPA check and performance samples. An overall description of the analysis using flame AAS, cold-vapor AAS or the heated graphite furnace techniques shows 2σ limits as follows:

Concentration	2σ Limits
Detection limit	± 200%
10 times detection limit	± 30%
100 times detection limit	± 10%

Table A.6-1

METALS IN POTW INFLUENT SCREENING SAMPLES

Concentration, µg/l

Metal	R	C	S	HA	W	L	CB	HB	CA
CR	16.	19.	5.	7.	10.	46.	300.	6.	13.
Cu	18.	24.	25.	31.	91.	120.	190.	31.	120.
Ni	6.	6.	1.	4.	1.	20.	150.	9.	5.
Zn	80.	540.	160.	120.	140.	500.	520.	60.	120.
Pb	18.	500.	38.	17.	13.	51.	610.	17.	16.
Cd	0.6	4.3	1.1	0.5	1.5	20.6	12.1	<0.5	7.3
Ag	<0.5	<0.5	<0.5	5.	0.6	<0.5	5.	12.	7.
Sb	<1.	2.	<1.	<1.	4.	<1.	<1.	<1.	<1.
Hg	<1.	2.	<1.	<1.	<1.	<1.	<1.	1.	10.
As	<1.	2.	<1.	<1.	2.	<1.	35.	<1.	1.
Be	0.1	<0.05	0.05	<0.05	<0.05	<0.05	0.01	0.05	0.1
Se	3.	<0.5	4.	3.	3.	3.	2.	4.	<0.5
Tl	<2.	<2.	<2.	<2.	<2.	<2.	<2.	<2.	<2.

Note: All data which are underlined were obtained by flame AAs; mercury data were obtained by flame-off AAS; all other data were obtained by graphite furnace AAS.

Ref. 1: "Sampling and Analysis Procedures for Sceening of Industrial Effluents for Priority Pollutants, "USEPA, EMSL Report dated March, 1977, Revised April, 1977.

KEY FOR TABLE A.6-1

R - Roanoke
C - Culpeper
S - Staunton
HA - Harrisonburg*
W - Waynesboro
L - Lynchburg
CB - Charlottesville-Moores Creek
HB - Harrisonburg*
CA - Charlottesville-Meadow Creek

*The two Harrisonburg samples were taken at different points in the influent stream. No large, systematic difference was observed.

Gaseous hydride generation techniques as utilized in arsenic and selenium analysis tend to have wider 2σ limits, but also are prone to systematic accuracy offsets usually toward less than 100% recovery of the sample.

Detection limits are those specified in EPA 1974 - Methods for Chemical Analysis of Water and Wastewater.

One can notice a significant difference between the analyses presented for the Culpeper influent screening analyses and the later data obtained during the intensive sampling phase. It is the opinion of both laboratories concerned that the differences are real. The wide variability is to be expected in grab sampling of a dynamic influent stream of this nature.

Interlaboratory calibration or split sample analysis was not performed.

A.7 PESTICIDES

Pesticides for the screening influent samples are shown in Figure A.7-1, a collection of GC chromatograms.

The only pesticide observed in the Richmond system influent was 19 ppb of p,p'-DDE. The sludge is representative of an integration and concentration of the solids entering the plant over some unknown time interval. As a result, a total of 4 pesticides were observed in the sludge phase, two at relatively high levels.

- o γ-BHC 619 ppb
- o p,p' -DDE 8077 ppb
- o Dieldrin 1655 ppb
- o Endrin 44 ppb

No PCB's were detected in any of the Richmond Samples.

At the Culpeper plant, Dieldrin was seen in the effluent (13 ppb) and the downstream sediment (10 ppb). Other pesticides observed in Culpeper phases were:

- o β -BHC - upstream sediment 11 ppb
- o Endosulfan 1 - sludge 48 ppb
  - water upstream 22 ppb
- o γ-BHC - downstream sediment < 10 ppb

No PCB's were observed in the Culpeper samples.

Pesticide QC Effort

A blind sample obtained from Applied Science Laboratories, Inc., State College, Pennsylvania was submitted to the laboratory for analysis. All three compounds were properly identified with response ratios to an external Aldrin standard as follows:

Heptachlor	92.5%
Aldrin	100%
Heptachlor Epoxide	96.2%

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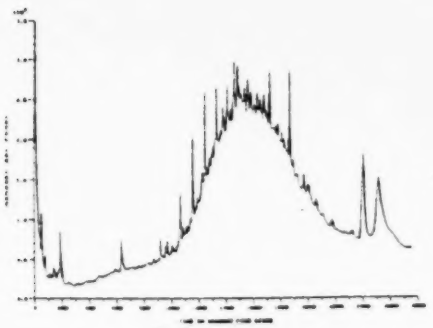
Figure A.7-1

Screening Influent Samples - Pesticide Chromatograms



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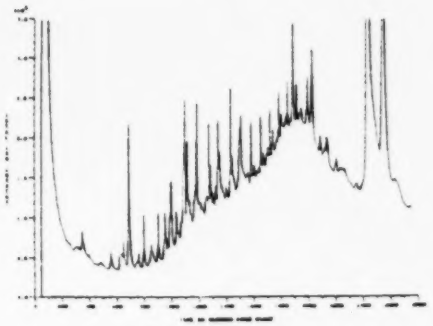
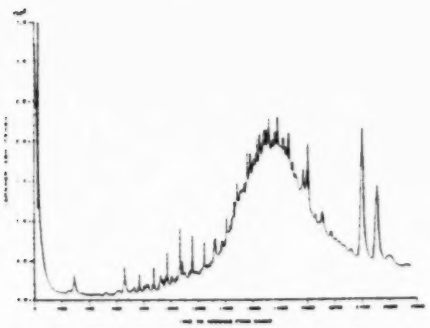
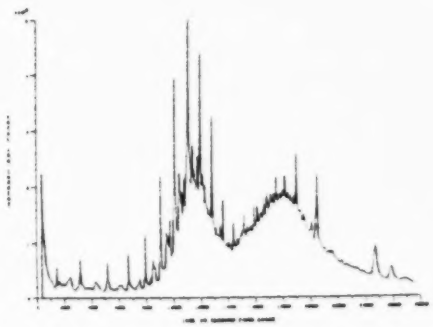


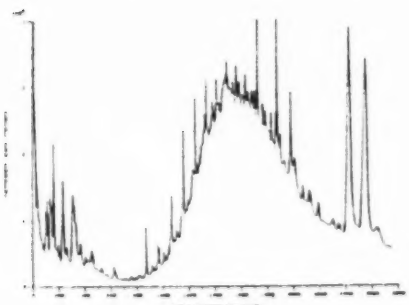
Lynchburg



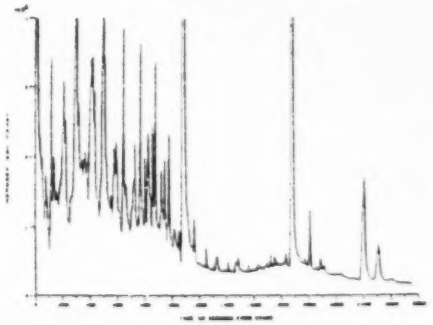
Charlottesville - Meadow Creek



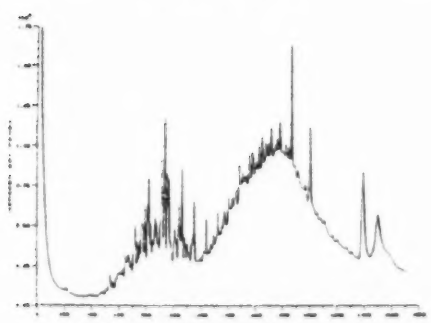
Charlottesville - Moore's Creek



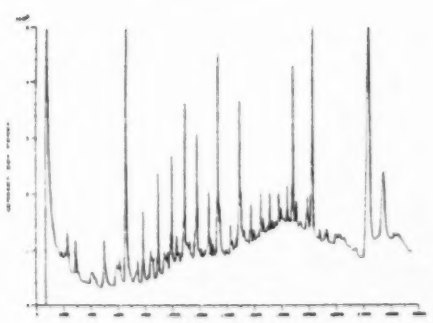
Harrisonburg



Waynesboro



Roanoke



Staunton

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APPENDIX A.8

MISCELLANEOUS PARAMETERS

Miscellaneous Parameters

The analyses completed in this set were mainly those classic parameters which have been used to describe POTWs in the past. These were measured only at Culpeper and Richmond in order that the solids and carbon loadings give an overall indication of the efficiency of removal process operating on the wastewater.

Quality control efforts on these parameters have been on going since the parameters are routinely measured during other on going projects. Examples of QC analysis follow in Table A.8.1.

TABLE A.8-1

TYPICAL QC RESULTS FOR ANALYSIS OF BLIND SAMPLES

Parameter	Laboratory No.	Amount Added	Amount Found	Percent Difference
COD	2405	50 ppm	58.6 ppm	+17.2
	2406	500 "	487.0 ppm	- 2.6
	2407	100 "	90.9 ppm	- 9.1
TOC	77	50.10 ppm	49.8 ppm	+ 0.59
	78	2.00 "	2.0 ppm	- 0
	79	100.2 "	96.6 ppm	- 3.59
NITRATE	147	0.119 ppm	0.13 ppm	+ 9.2
	148	0.998 "	0.95 ppm	+ 4.8
	150	0.80 "	0.77 ppm	+ 3.7
Total Phosphorus	2466	2.0 ppm	2.0 ppm	0
	2467	1.0 "	1.06 ppm	+ 6.
	2468	0.396	0.43 ppm	+ 8.5
	2470	0.6	0.56 ppm	+ 6.6

VOA TIME STUDY

In an attempt to explore the effects of prolonged storage on the concentrations of volatile organics in water for VOA analysis a time study was performed. A total of 5 duplicates of Culpeper Influent were prepared in the field for VOA analysis. One was analyzed on the day after sampling, and the next three at intervals of 7, 14 and 21 days after sampling. The last sample was held for 35 days since the analysis of the other 4 samples revealed little loss of volatiles up to 21 days.

The data is shown in Table 6.0.1.

In order to interpret the data one must know the precision of the analytical technique. The following information is available from an earlier set of VOA analysis accomplished during the same working day as shown below.

	(a)	(b)	(c)	Av.	Average Difference as % of mean
CHLOROFORM (ppb)	13	11	10	11.3	8.1
TOLUENE (ppb)	22	13	21	18.66	20.3
TETRACHLORETHYLENE (ppb)	571	510	438	506	9.0
1,2-DICHLOROETHYLENE (ppb)	11	12	10	11	6.1

Without sufficient replication for good statistical analysis, we can still examine the total bandwidth about the mean value. In only one case of the four above does the average difference from the mean value exceed 10%. In part this is due to the data which appears at roughly 10X the 1 ppb detection limit. From 10X down to the detection limit the data is usually reported in 1 or 0.5 ppb steps. For that reason, the 1,2-dichloroethylene data could conceivably cover a range from 9 to 13, which would double the % Average Difference to about 12%.

With the small amount of information available on both analytical precision and VOA solution stability, it may be considered that ± 20% in the 10-100 ppb range to be an estimate of overall precision. By using the first four time study data points for 1,1,2,2-tetrachloroethylene, chloroform and ethyl-benzene, one calculates relative standard deviations of 22.6%, 18.2% and 20.2% respectively.

The reasonable conclusion is that these compounds and the toluene were stable for analysis over the 21 day storage time, and that the variations were within the error band of the measurement technique.

These conclusions should not be wantonly extrapolated to other matrices to be analyzed for volatile organics, but every effort should be made to extend our understanding of matrix effects on such analysis.

Table B-1 provides the data obtained for the time study. In Figure B-1 we see a loss of low concentration compounds over the course of the study.

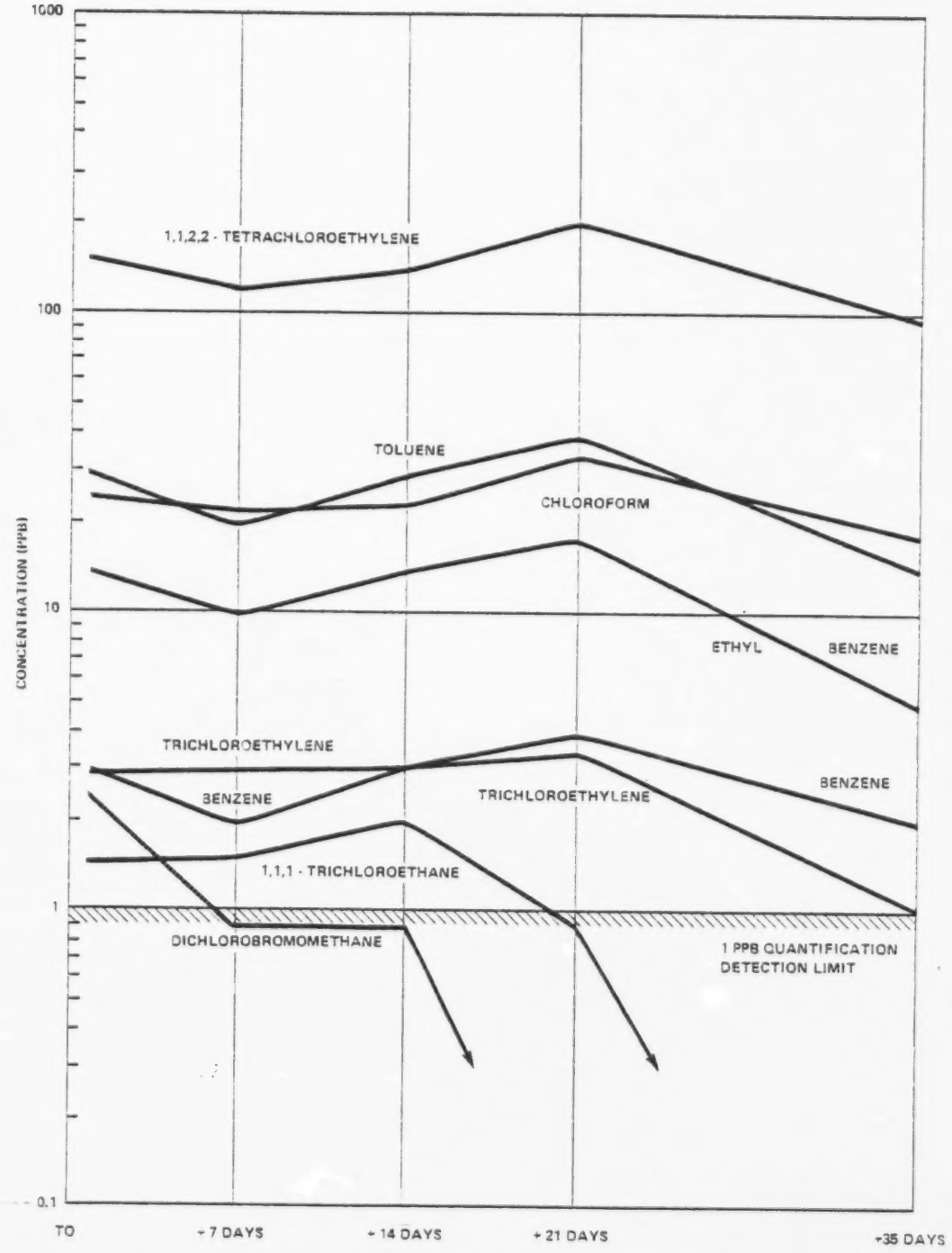
TABLE B-1

VOA TIME STUDY

CONCENTRATION (ppb)

NO.	NAME	1 DAY	7 DAYS	14 DAYS	21 DAYS	35 DAYS	Using First 4 Data Points: σ as % of Mean	Using First 4 Data Points: |σ| (ppb)
49	DICHLOROBROMOMETHANE	2.5	< 1	< 1	ND	ND		
51	CHLOROFORM	25	22	23	34	18	18.2%	4.7
58	1,1,1-TRICHLOROETHANE	1.5	1.5	2	ND	ND		
65	TRICHLOROETHYLENE	3	3	3	3.5	1		
66	1,1,2,2-TETRACHLOROETHYLENE	157	121	140	216	96	22.6%	35.5
78	BENZENE	3	2	3	4	2		
85	ETHYL BENZENE	14	10	14	18	5	20.2	2.83
87	TOLUENE	29	20	29	39	13	34	8.85

FIGURE B-1
VOA TIME STUDY



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APPENDIX D
INDUSTRIES LOCATED IN POTW CITIES SAMPLED

The following are Dun & Bradstreet data listings for the cities sampled in the screening and intensive phases of this work. No distinction is made in these listings between direct dischargers or those who may discharge to the POTW.

	Industrial Category	# Plants	Total Employees
CULPEPER			
01	Timber Products Processing	2	30
04	Iron & Steel Manufacturing	1	250
07	Textile Mills	3	273
11	Paint & Ink Formulation and Printing	4	50
18	Machinery & Mechanical Products Manufacturing	6	216
22	Not Classified on Consent Decree	10	466
RICHMOND			
01	Timber Products Processing	22	350
03	Leather Tanning & Finishing	3	106
04	Iron & Steel Manufacturing	1	59
06	Inorganic Chemicals Manufacturing	4	151
07	Textile Mills	41	3246
09	Non-Ferrous Metals Manufacturing	3	140
10	Paving & Roofing Materials (Tars & Asphalt)	1	4
11	Paint & Ink Formulation and Printing	142	5503
13	Auto and other Laundries	1	26
14	Plastic and Synthetic Materials Manufacturing	2	3509

Industrial Category		# Plants	Total Employees
RICHMOND (Cont'd.)			
15	Pulp & Paperboard Mills, Converted Paper Products	34	3390
16	Rubber Processing	6	750
17	Miscellaneous Chemicals	19	1729
18	Machinery & Mechanical Products Manufacturing	197	9832
19	Electroplating	11	150
22	Not Classified on Consent Decree	204	21,297
CHARLOTTESVILLE			
01	Timber Products Processing	6	186
03	Leather Tanning & Finishing	1	2
05	Petroleum Refining	1	11
07	Textile Mills	6	824
11	Paint & Ink Formulation and Printing	14	686
15	Pulp & Paperboard Mills, Converted Paper Products	3	17
17	Miscellaneous Chemicals	2	8
18	Machinery & Mechanical Products Manufacturing	31	2693
22	Not Classified on Consent Degree	18	721
ROANOKE			
01	Timber Products Processing	11	233
03	Leather Tanning & Finishing	1	1
04	Iron & Steel Manufacturing	2	402
07	Textile Mills	12	4460
10	Paving and Roofing Materials (Tar & Asphalt)	1	3
11	Paint & Ink Formulation, Printing	24	1003

Industrial Category		# Plants	Total Employees
ROANOKE (Cont'd.)			
14	Plastic & Synthetic Materials Manufacturing	1	32
15	Pulp & Paperboard Mills, Converted Paper Products	7	555
17	Miscellaneous Chemicals	1	20
18	Machinery & Mechanical Products Manufacturing	62	2859
22	Not Classified on Consent Decree	61	3643
HARRISONBURG			
07	Textile Mills	5	582
11	Paint & Ink Formulation and Printing	8	198
15	Pulp & Paper Mills, Converted Paper Products	1	136
18	Machinery & Mechanical Products Manufacturing	17	2157
22	Not Classified on Consent Decree	28	1210
LYNCHBURG			
01	Timber Products Processing	6	58
03	Leather Tanning & Finishing	4	866
07	Textile Mills	9	2080
11	Paint & Ink Formulation and Printing	17	913
15	Pulp & Paperboard Mills, Converted Paper Products	1	100
16	Rubber Processing	3	164
17	Miscellaneous Chemicals	1	290
18	Machinery & Mechanical Products Manufacturing	42	7703
19	Electroplating	2	47
22	Not Classified on Consent Decree	33	1661

Industrial Category		# Plants	Total Employees
STAUNTON			
01	Timber Products Processing	3	61
07	Textile Mills	3	542
11	Paint & Ink Formulation and Printing	4	71
18	Machinery & Mechanical Products Manufacturing	13	1302
22	Not Classified on Consent Decree	10	190
WAYNESBORO			
01	Timber Products Processing	2	9
06	Inorganic Chemicals Manufacturing	1	1
07	Textile Mills	2	3392
11	Paint & Ink Formulation and Printing	4	96
14	Plastic & Synthetic Materials Manufacturing	3	3405
17	Miscellaneous Chemicals	1	1
18	Machinery & Mechanical Products Manufacturing	19	3124
19	Electroplating	1	3
22	Not Classified on Consent Decree	8	517